İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

HYDROGEN FUEL CELL POWERED ELECTRIC VEHICLES AND AN APPLICATION OF IMPROVEMENT FOR THE DESORPTION EFFICIENCY OF A METAL HYDRIDE STORAGE

M.Sc. Thesis by
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Programme : Mechatronics Engineering

FEBRUARY 2011

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Date of defence examination: 28 January 2011

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FEBRUARY 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

HİDROJEN YAKIT HÜCRELİ ELEKTRİKLİ ARAÇLAR VE METAL HİDRİD HİDROJEN SAKLAMA ORTAMLARININ SALIVERME VERİMİNİN İYİLEŞTİRİLMESİ

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Tezin Enstitüye Verildiği Tarih : 20 Aralık 2010
Tezin Savunulduğu Tarih : 28 Ocak 2011

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ŞUBAT 2011

FOREWORD

Firstly, I would like to express my deep appreciation and thanks for my advisor Dr. Azmi DEMİREL as he allowed me to work with him for the second time and he provided me with his own materials for experimental setup; the Metal Hydride Hydrogen Storage and the PEM Fuel Cell. Secondly, I would like to thank to my managers and my colleagues from Alarko-Carrier R&D Department and TUPRAS-İzmit Refinery Maintenance Department for all their support. Thirdly, I would like to thank to Zeynep KARA, Jose Manuel MORELL, Fikri ELMAS and Sami KÖSEOĞLU for helps on writing and experimental setup. Lastly, I would like to thank to my wife, Ayfer KIVRAK, as she always with me during this hard period.

December 2010

Mehmet Fatih KIVRAK
Electrical Engineer

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ABBREVIATIONS

PV	: Photovoltaics
CEV	: Combustion Engine Vehicles
EV	: Electrical Vehicles
HEV	: Hybrid Electrical Vehicles
BDC	: Brushed Direct Current
PEFC	: Polymer Electrolyte Fuel Cell
PEMFC	**:** Proton Exchange Membrane Fuel Cell
AFC	: Alkaline Fuel Cell
PAFC	: Phosphoric Acid Fuel Cell
MCFC	: Molten Carbonate Fuel Cell
SOFC	: Solid Oxide Fuel Cell
LH_2	: Liquid Hydrogen
LTH	: Low Temp Hydride
HTH	: High Temp Hydride
LHV	: Lower Heating Value
LPG	: Liquid Petroleum Gas
SEC	: Specific Energy Consumption
MH	: Metal Hydride
TM	: Transition Metal
Non-TM	: Non-Transition Metal
CN	: Carbon Nanotubes
SWNT	: Single Walled Carbon Nanotubes

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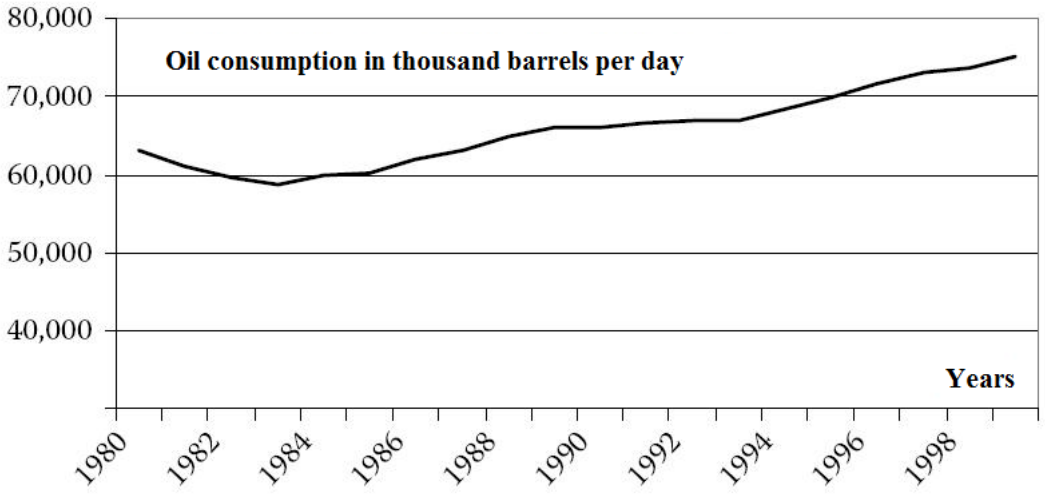
HYDROGEN FUEL CELL POWERED ELECTRIC VEHICLES AND AN APPLICATION OF IMPROVEMENT FOR THE DESORPTION EFFICIENCY OF A METAL HYDRIDE STORAGE

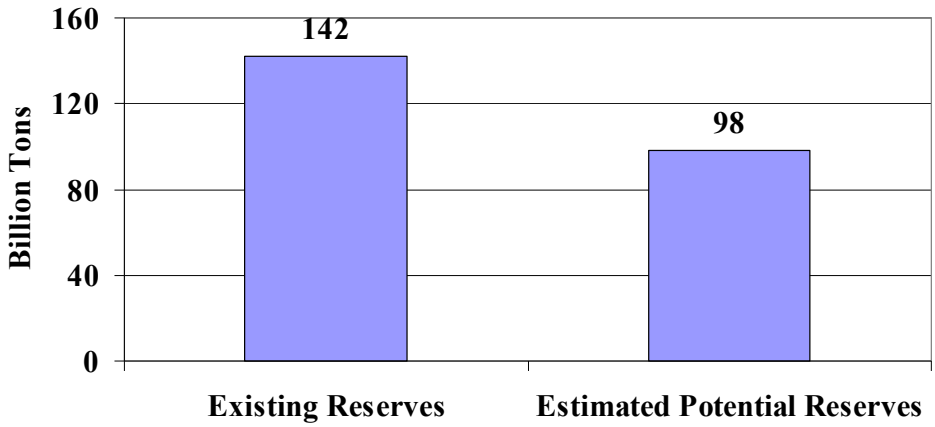
SUMMARY

Transportation is one of the main needs of people. This need may be occur for different reasons. These are sometimes obligations like going to work or school, but sometimes optional like going abroad. Whatever the reason is, the requirement must be provided by vehicles. Among various vehicle options, automobiles are the most demanded ones because of their features such as being comfortable, individual and practical, especially, in short distances. By the help of improving technology, different technical features, various motor powers, visual designs and comfort options are presented for people in a wide range of prices beginning with a few thousands dollars to millions. Developments started in 1769 when French engineer Nikolas-Joseph Cugnot had designed a vehicle, which could be considered as a prototype of existing automobiles. The vehicle had three wheels, it was driven by steam power and its maximum speed was 3.6 km/h. However, steam powered vehicles were not preferred, since they had many disadvantages such as higher temperature, explosion and noise (Demirel, 1995). Turning point of the automobile industry is 1876, because German engineer Otto invented four stroke internal combustion engine. In 1893 another German engineer Rudolf Diesel developed a new type of engine which is called with his surname, Diesel motor, to find more economic solution instead of gasoline engine. In 2000s requirements for finding cheaper solution, LPG has been started to use on automobiles. All of these three alternatives have different advantages or disadvantages when compared with each other, but they have a common and important problem that they consume fossil fuels.



Shortage of fossil fuels and harmful effects' have become main problem of today's world. The share of transportation in fossil fuel usage is 32% and daily oil

consumption has been increasing. These causes force people to find new clean energy sources for vehicles to decrease pollutant gas emissions such as solar energy, biofuels and hydrogen energy. There is an opportunity to convert solar energy to electrical by photovoltaics but a photovoltaic panel which has ability to run a typical four wheel automobile, should have very large surface area (Demirel, 1991). Likewise, they are sensitive for air conditions and still expensive. These disadvantages make solar vehicles inconvenient for vehicles. Another alternative energy source is biofuels, which have been searched in recent years but they are now used as an additive, for example, bioethanol is added to gasoline to increase octane and biodiesel is added to diesel to improve performance and decrease particles. They have positive effect on emissions but their cost is still expensive. Thirdly, hydrogen is one of the major clean energy sources according to its critical specifications: it has very high energy potential and it is the most abundant element in the universe. When compared with fossil fuels, heat combustion energy of hydrogen equals third times of methane or five times of coal (Selvam, 1986).

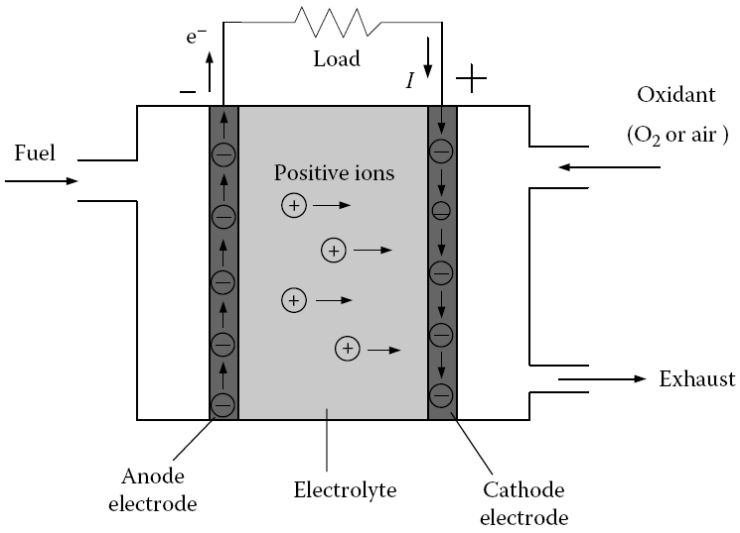


Hydrogen is used by fuel cells, which have ability to generate electrical energy without combustion. A fuel cell needs oxygen and hydrogen to generate electricity, besides the reaction produces water. Whereas, exhaust gases of conventional motors contain carbon dioxide (CO_2), nitrogen compounds (NO_x), sulfur compounds (SO_x) and carbon monoxide (CO) which are corruptive for atmosphere and human health, directly or indirectly. There are five types of fuel cells: PEMFC, AFC, PAFC, MCFC and SOFC. PEMFCs are considered as the most appropriate type for electrical vehicles since their operating temperature is low and their start up and response abilities are good (EG&G Technical Services Inc., 2004).

Electrical energy created by a fuel cell can be used with or without a power electronic circuit to run an electrical motor. Power electronics controllers set voltage and current to run an electric motor at desired speed and torque. Therefore, electric vehicles do not need any transmission mechanisms and necessary transmission oils. Another benefit of electric motors is running quieter than IC motors. Moreover, their energy conversion efficiency is higher than IC motors (Ehsani, 2010).

Future of fuel cell systems mainly depend on hydrogen production and storage systems. For present system, fossil fuels are refined in central plants and distributed to oil stations. People can get required fuel from these stations, easily. As a result, advanced hydrogen production and storage systems must be feasible to be

commercial, like existing fuel systems. Low-emission and high-efficiency vehicles need compact production and storage systems to take place of ICVs.



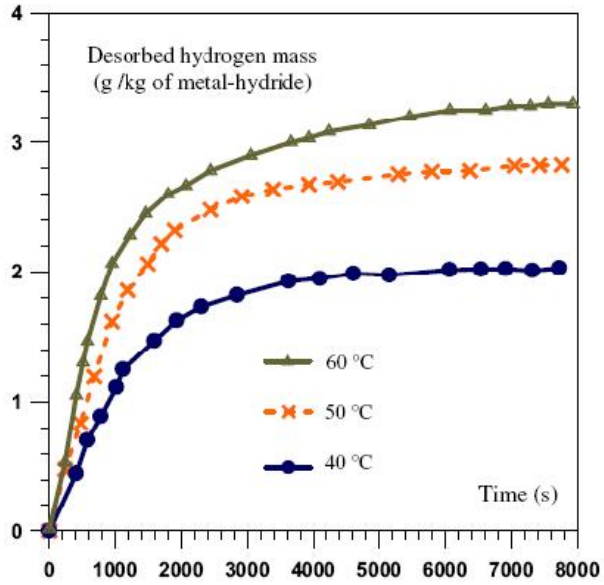
Sir William Grove invented the fuel cell in 1839, but it just started to spread because of higher material costs. Now, the cost of cell material components is decreasing. However, the future of fuel technology mainly depends on hydrogen production and storage systems as mentioned above. When viewed from this aspect, hydrogen production becomes the first issue. Since the water covers 70% of the world surface, it is the first option in researchers mind. There are many ways to separate water into hydrogen and oxygen atoms such as electrolysis, photovolatics, photobiologic and high-temperature method (Riis, 2005). Another option is producing hydrogen from fossil fuels as they consist of carbon and hydrogen. This method is commonly preferred by refineries to provide their hydrogen need. On the other hand, this method requires high-temperature and it produces CO_2 about ten thousand tons per year. The last method is oxidation of organic substances but again, reaction produces CO and CO_2. It can be derived that if the aim of hydrogen energy is decreasing the pollutant emissions, the water seems as the best option to produce hydrogen.

Production of hydrogen must be handled in central plants like conventional fossil fuel systems because the process is complex and must be operated carefully. The other important point is the storage of hydrogen. As hydrogen is in gas form at ambient temperature, it can be pressurized and stored in tanks. Generally, hydrogen is compressed at 200-350-700 bars in carbon fiber jacketed aluminum tanks. On the other hand, it will be very dangerous to keep a 700 bar tank in a vehicle trunk. Any fault of production and any car accident can cause critical problems. Another storage method is liquid hydrogen at – 270 ^{o}C in well-insulated cryogenic tanks (Gardiner, 2009). Similarly, liquefied hydrogen has serious safety problems because there will be wide differences between ambient temperature and liquid tank temperature. Any car accident can damage the insulated tank and because of the temperature difference, hydrogen tends to expand which causes powerful explosions. Furthermore, energy conversion efficiency of both storage options is low. Because, compression energy equals typically 20% of Lower Heating Value (LHV) and liquefaction energy equals 40% of LHV.

At this point, pressurized and liquefied hydrogen storage systems seem not applicable for electrical vehicles. As a result, the last option becomes solid hydrogen

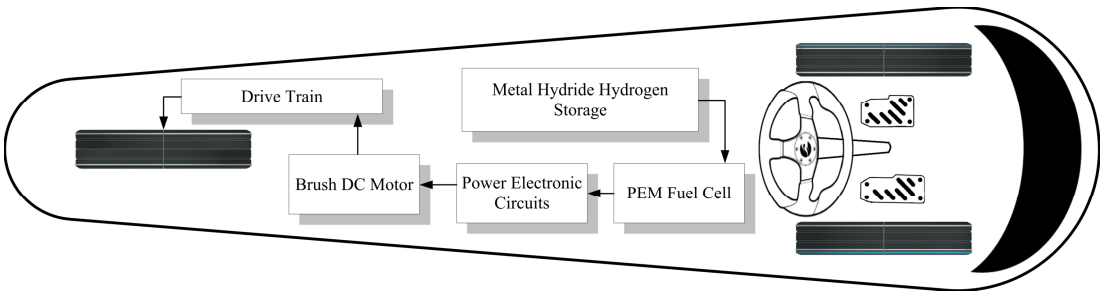
storage systems. Carbon and other high surface area materials can store hydrogen by Van Der Waals interconnection in solid space. The process is also called physisorption, which suffers from lower storage capacity and poor reversible characteristics (Ströbel, 2006). There is another way to store hydrogen in solid form, metal hydrides. The operating temperature and pressure of metal hydrides is low enough to use them in vehicles. Moreover, their reversible performance and gravimetric storage capacity are good. When compared with other hydrogen storage systems, it can be seen that metal hydrides seem as the best option for electrical vehicles by their beneficial features.

Hydrogen absorption and desorption by a metal hydride is a thermo-chemical reaction. The absorption characteristic is exothermic and the desorption characteristics is naturally endothermic. During absorption, metal hydride storage heats up so if it is cooled on absorption, absorbed hydrogen quantity will increase (Dhaou, 2009). Similarly, during desorption, metal hydride storage cools down so if it is heated on desorption, desorbed hydrogen amount will increase.

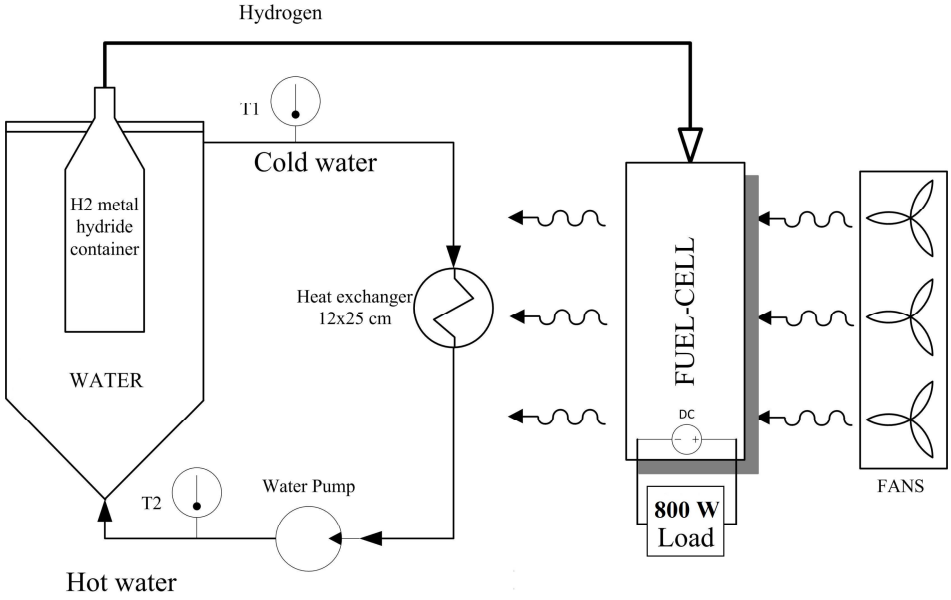


Metal hydrides are energy storage and conversion systems. Like every energy conversion system, there is a difference, which means loss, between absorbed and desorbed hydrogen quantity. It is not possible to discharge all absorbed hydrogen because of losses (Forde, 2009). Heating on desorption increases the desorbed hydrogen amount, as a result desorption efficiency increases. When compared with normal operation, heating on desorption will reduce the required weight and volume of hydrogen storage to run particular range. In other words, enabling to get more hydrogen from the same storage by heating system, the total range of the vehicle could be improved.

In this study, it is aimed that improving the desorption efficiency of a fuel cell vehicle's hydrogen storage. The fuel cell vehicle has three wheels and powered by a brush type DC motor, which is mounted on backside of the vehicle. Block scheme of the vehicle is given below. The vehicle's fuel cell type is PEM, which is sourced by a group of metal hydride hydrogen storage.



To improve the desorption efficiency of the metal hydride storage; a closed-circuit heat transfer system was designed. The block scheme of the system is given below Figure. For normal operation, a group of fan force cold air that is sucked in ambient atmosphere, to fuel cell fins. While cold air passes through the fins, it absorbs the fuel cell's heat and hot air removed from the fuel cell. In this study, a typical car radiator, which was used as a heat exchanger, was fitted on hot-air exit of the fuel cell. One of the metal hydride storage was put into a vessel. The vessel had holes to enable hydrogen outlet and water inlet-outlet. Water outlet of the vessel was connected to radiator water inlet through the water pump. Water inlet of the vessel was connected to radiator water outlet. A plastic housing water pump was used to circulate water in this closed circuit. The aim of this system was taking hot air's heat, which was removed from fuel cell, and transferring it to the vessel. By this way, metal hydride storage would be heated up during desorption.



The experiments showed that proposed system significantly increased the desorbed hydrogen amount from the metal hydride storage. The metal hydride storage was tested with and without proposed system while the PEM fuel cell was supplying 800 W output power. The storage could supply hydrogen for 61 minutes with proposed system, on the other hand; it could supply only 18 minutes without proposed system. Although it was supposed by PEMFC that metal hydride storage is empty, the last experiment showed, in reality, there was still some hydrogen in the storage.

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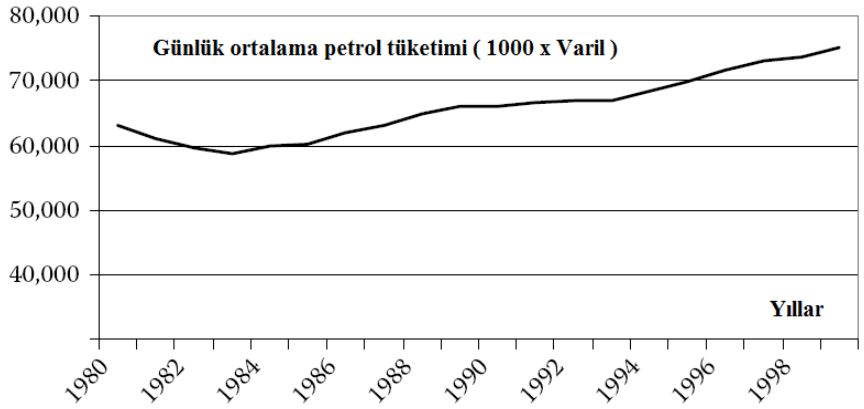
HİDROJEN YAKIT HÜCRELİ ELEKTRİKLİ ARAÇLAR VE METAL HİDRİD HİDROJEN SAKLAMA ORTAMLARININ SALIVERME VERİMİNİN İYİLEŞTİRİLMESİ

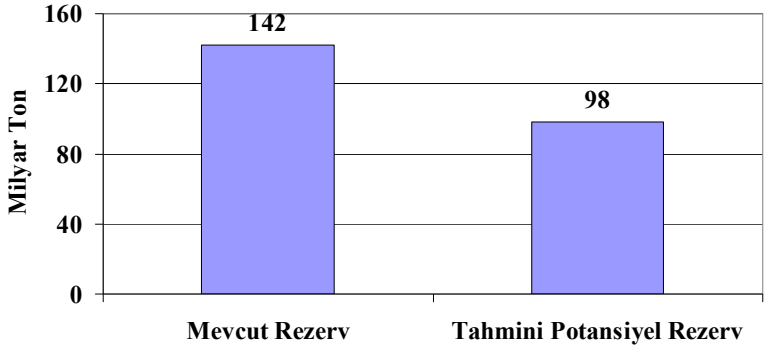
ÖZET

Ulaşım, içinde bulunulan yüzyılda insanlarının en temel ihtiyaçlarından biri olarak ortaya çıkmaktadır. İnsanlar çok farklı sebeplerle bir yerden başka bir yere gitme ihtiyacı hissederler. Kimi zaman bu sebep evden işe veya okula gitmek gibi zaruri; kimi zaman da gezi için bir ülkeden başka bir ülkeye gitmek gibi öznel de olabilmektedir. Sebebi ne olursa olsun kişilerin veya nesnelerin yer değiştirme ihtiyacı için çeşitli ulaşım vasıtaları kullanılmaktadır. Farklı ulaşım seçenekleri arasında otomobiller, konforlu, bireysel ve bilhassa yakın mesafelerde pratik olmalarından dolayı en yaygın ve en çok tercih edilen seçenek olmuştur. Gelişen teknoloji ile birlikte farklı teknik donanımlar, farklı motorlar, farklı görsel tasarımlar ve ya farklı konfor seçenekleri; bir kaç bin dolardan başlayıp milyon dolarlara kadar uzanan bir yelpazede insanların beğenisine sunulmaktadır. Bu gelişimin temeline gidildiğine 1769 tarihi öne çıkmaktadır. Çünkü bu tarihte Fransız Nikolas-Joseph Cugnot mevcut araçların temeli kabul edilebilecek buharlı, üç tekerli, maksimum hızı 3.6 km/saat olan bir otomobil geliştirmiştir, fakat buharlı otomobiller; yüksek sıcaklık, patlama riski ve gürültü gibi bir takım olumsuz yönlere sahip olmalarından dolayı tercih edilmemiştir (Demirel, 1995). Otomobil tarihinin ikinci ve belki de gerçek miladı Alman mühendis Otto'nun, benzinli, dört zamanlı, içten yanmalı motoru geliştirdiği 1876 tarihidir. 1893'te ise başka bir Alman mühendis Rudolf Diesel, günümüzde soyadı ile özdeşleşen motor tipinin mucidi olarak Otto'nun benzinli motoruna ekonomik bir alternatif geliştirmiştir. 1800'lü yıllardan başlayarak 2000'li yıllara gelindiğine benzinli ve motorinli araçların pazara hakim olduğu görülmektedir. Bu dönem içinde, daha ekonomik bir çözüm olarak LPG'li araçlar da sahneye çıkmıştır. İster benzinli, ister motorinli, isterse de LPG'li olsun, birbirine göre çeşitli üstünlükleri bulunan bu otomobillerin hepsinin müşterek ve en önemli problemi fosil yakıt tüketmeleridir.



Fosil yakıtların kıtlığı ve üretilmelerinden tüketilmelerine kadar olan çevrimde doğaya olan zararlı etkileri, güncel dünyanın karşılaştığı en büyük problemlerinden biri haline gelmiştir. Fosil yakıtların %32'sinin motorlu araçlar tarafından

kullanılması ve günlük yakıt tüketiminin hızla artması; insanları, fosil yakıt yerine, üretiminde ve tüketiminde zararlı gaz yayılımını azaltan veya tamamen ortadan kaldıran, doğal ve temiz enerji kaynaklarını araçlarda kullanmaya yöneltmiştir. Güneş enerjisi, bio-yakıtlar ve hidrojen enerjisi bu alternatiflerin en önemlileridir. İlk olarak, güneş pilleri ile üretilen elektrik enerjisi yüksek verimli ve sıfır yayılımlı bir elektrik motorunu besleyebilmektedir. Fakat ortalama bir aracı ortalama bir performans ile yeterli bir menzilde hareket ettirebilecek kapasitede bir güneş pili çok büyük bir yüzey alanına ihtiyaç duymaktadır (Demirel, 1991). Bununla birlikte maliyetlerinin çok olması, depolama özelliklerinin olmaması ve hava şartlarından çok fazla etkilenmeleri güneş enerjili otomobillerin ticarileşmesinin önünde büyük bir engel olarak durmaktadır. Son yıllarda üzerinde durulan bir diğer alternatif enerji kaynağı bio-etanol, bio-dizel gibi bio-yakıtlardır. Bu yakıtlar mevcut uygulamalarda oktanı yükseltmek için benzine, performansı arttırmak ve partikülleri azaltmak için amacıyla motorine katkı maddesi olarak eklenmektedir. Pahalı olmaları, sıfır yayılımlı olmamaları bu yakıtların olumsuz yanları olarak göze çarpmaktadır. Bununla birlikte sürdürülebilir sistemde yayılımı ve kirliliği azaltacağı da mutlaktır. Araştırmacıların üzerinde yoğunlaştığı en önemli alternatif ise hidrojendir. Çünkü hidrojen yüksek enerji potansiyeline sahip evrendeki en yaygın elementtir. Fosil yakıtlarla kıyaslandığında hidrojenin ısıl enerjisi metanın 3 katına, kömürün ise 5 katına eşittir (Selvam, 1986).

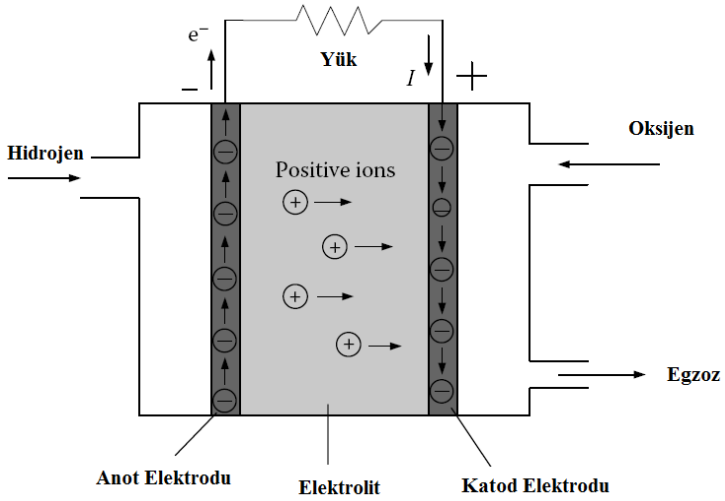


Hidrojenin, doğaya zararlı her hangi bir salınım olmadan, sadece su buharı yayan ve yakıt hücresi olarak adlandırılan sistemlerde kullanılması sonucunda elektrik enerjisi üretilebilmektedir. Yakıt hücrelerinde, hidrojen ve oksijen molekülü tepkimeye girmekte, bu tepkime sonucunda elektrik enerjisi ve atık olarak, su üretilmektedir. Oysa ki geleneksel içten yanmalı motorların atık gazları karbon dioksit, karbon monoksit, azot ve kükürt gibi doğaya ve insanlara, doğrudan veya dolaylı zararlı gazlar ihtiva etmektedir. Alkalin (AFC), Fosforik Asitli (PAFC), Erimiş Karbonatlı (MCFC), Katı Oksit (SOFC) gibi yakıt hücreleri ile kıyaslandığında, polimer elektrolit membran yakıt hücreleri (PEMFC), düşük çalışma sıcaklıkları, yüksek akım-gerilim kapasiteleri ve hızlı kalkış/yanıt süreleri ile otomobil uygulamaları için en uygun çözüm olarak görülmektedir (EG&G Technical Services Inc., 2004).

Yakıt hücresi tarafından üretilen elektrik enerjisi bir güç elektroniği çeviricisi ile elektrik motorunu beslemek için kullanılabilir. Aynı zamanda uygulanan elektrik enerjisinin gerilim/akım gibi parametreleri değiştirilerek hız-moment ayarı yapılabilir. Bu sayede, ilave bir şanzıman sistemi ve bu sistemin ihtiyaç duyduğu yağlara da gerek kalmayacaktır. Elektrik motorları, içten yanmalı motorlarla kıyaslandığında; yüksek verime ve güvenilirliğe sahiptir (Ehsani, 2010). Ayrıca

antifriz, yağ değişim ihtiyacı da yoktur. Sunduğu performans avantajları ve sıfır-salınım özelliği elektrik motorunu tercih sebebi yapmaktadır.

Yakıt hücrelerinin, otomotiv uygulamalarında kullanılabilir olması, başta hidrojen depolama sistemleri olmak üzere, hem üretim hem de depolanma sistemlerinin gelişmesine bağlıdır. Güncel teknolojide, fosil otomobil yakıtları büyük rafinerilerde işlenmekte, sıvı veya gaz olarak istasyonlara dağıtılmaktadır. Sürücüler otomobillerinin depolarına ihtiyaç duydukları kadar yakıtı kolayca, bu dağıtım istasyonlarından almaktadırlar. Yayılımsız ve yüksek verimle çalışan elektrikli araçların, içten yanmalı araçların yerini alabilmesi için mevcut sistemler gibi, sorunsuz üretim ve depolama sistemlerine sahip olması gerekmektedir.



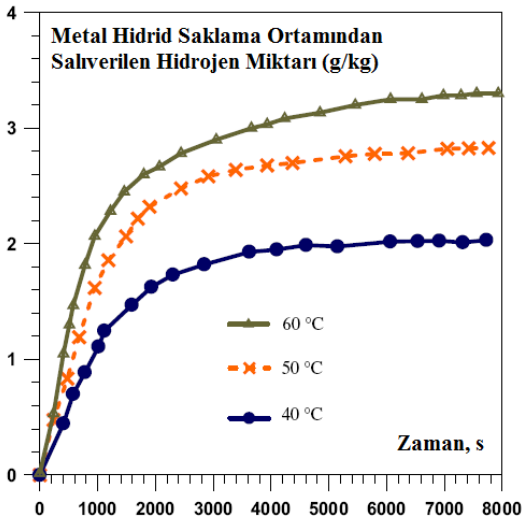
Yakıt hücresi ilk olarak 1839'da Sir William Grove tarafından geliştirilmiş, fakat malzeme fiyatlarının yüksek olması nedeniyle ancak bu yüzyılda yaygınlaşmaya başlamıştır. Bu noktadan sonra, yakıt hücrelerinin kullanılabilmesi, büyük ölçüde hidrojen üretim ve depolama teknolojilerine bağlıdır. Hidrojen, yapısında bulunduğu sudan, fosil yakıtlardan veya organik bileşiklerde üretilebilmektedir. Dünyanın %70'inin sularla kaplı olması, hidrojen üretiminde akla ilk olarak suyu getirmektedir. Elektroliz, foto-voltaik sistemler, foto-biyololik sistemler ve aşırı yüksek sıcaklık sudan hidrojen üretilmesinde kullanılan yöntemlerdir (Riis, 2005). Bunun dışında, bir karbon-hidrojen bileşiği olan fosil yakıtlardan da hidrojen elde etmek mümkündür, fakat yüksek sıcaklık gereksinimi ve reaksiyon sonucunda karbon dioksit oluşması, bu seçeneğin olumsuz yanları olarak öne çıkmaktadır. Son olarak, organik maddelerin oksitlenmesi veya bir grup bakteri tarafından kullanılması sonucu hidrojen üretme imkanı da vardır. Keza bu yöntem sonucunda da karbondioksit ve karbon monoksit açığa çıkmaktadır.

Hidrojen üretimindeki zorluklar, petrolün merkezi rafinerilerde işlenmesi gibi hidrojenin de merkezi üretimini zorunlu hale getirmektedir. Bunun yanında bir diğer zorunluluk hidrojenin otomobil içinde depolanması durumudur. Normal şartlarda gaz halinde bulunan hidrojen, 200-350 veya 700 bar basınç altında karbon fiber destekli alüminyum tanklarda, -270 ^{o}C de ise sıvı olarak, üst seviye yalıtımlı kaplarda saklanabilmektedir (Gardiner, 2009). Her iki alternatifin de enerji yoğunluğu yüksek olmasına rağmen, basınçlandırma veya soğutma için gereken enerji miktarları, sistem verimlerini düşürmektedir. Ayrıca, 700 bar basınçtaki hidrojen tankının veya dış ortamla arasında 300 ^{o}C sıcaklık farkı bulunan hidrojen dolu bir kabın araç içinde taşınması son derece risklidir. Bu olumsuzluklara, imalat ve tesisattaki hatalar ve

bilhassa araç kazaları eklendiğinde; hidrojenin araçlarda gaz veya sıvı olarak depolanması mümkün görünmemektedir.

Bu bilgiler ışığında, araçlarda hidrojenin gaz veya sıvı olarak depolanmasının uygun olmadığı anlaşılmaktadır. Bu durumda son alternatif hidrojenin katı ortamlarda depolanmasıdır. Karbon malzemeler ve metal hidridler hidrojenin depolanabildiği katı ortamlardır. Hidrojenin karbon ve diğer geniş yüzeyli atom ve moleküller tarafından depolanması, zayıf Van Der Waals bağları ile sağlanmaktadır (Ströbel, 2006). Düşük enerjili bu bağlar sayesinde hidrojen, bu maddelerin yüzeyine tutunmak suretiyle depolanabilmektedir. Depo kapasitelerinin ve çift yönlü reaksiyon kabiliyetlerinin düşük olması, bu materyallerin araçlarda kullanılabilme ihtimalini düşürmektedir. Bu sebeple, düşük sıcaklıkta ve basınçta çalışan metal hidrid saklama ortamları araç uygulamaları için en uygun çözüm olmaktadır. Ayrıca, tersinir karakteristikleri ve depolama miktarları, karbon ve diğer geniş yüzeyli atom ve moleküllerden daha iyidir. Bu özellikleri, metal hidrid saklama ortamlarını, elektrikli otomobillerde ticari anlamı olan uygulamalar için bir seçenek haline getirmektedir.

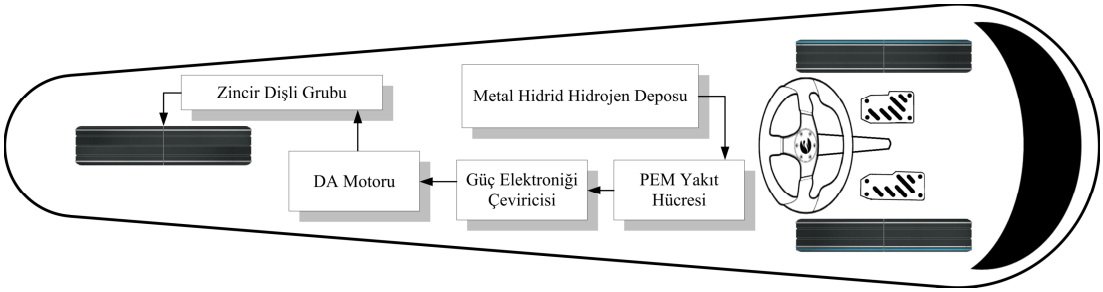
Hidrojenin metal hidrid depoya doldurulması ve depodan boşaltılması termokimyasal bir olaydır. Hidrojen emilimi ekzotermik, salıverilmesi ise endotermik karakteristiğe sahiptir. Emilim esnasında, hidrid deponun yaydığı ısı alındığında, başka bir deyişle depo soğutulduğunda; reaksiyon hızlanmakta, emilen hidrojen miktarı artmaktadır (Dhaou, 2009). Reaksiyon çift yönlü olduğu için, salıverme esnasında hidrid depo ısıtıldığında; reaksiyon yine hızlanmakta, salınan hidrojen miktarı da artmaktadır.



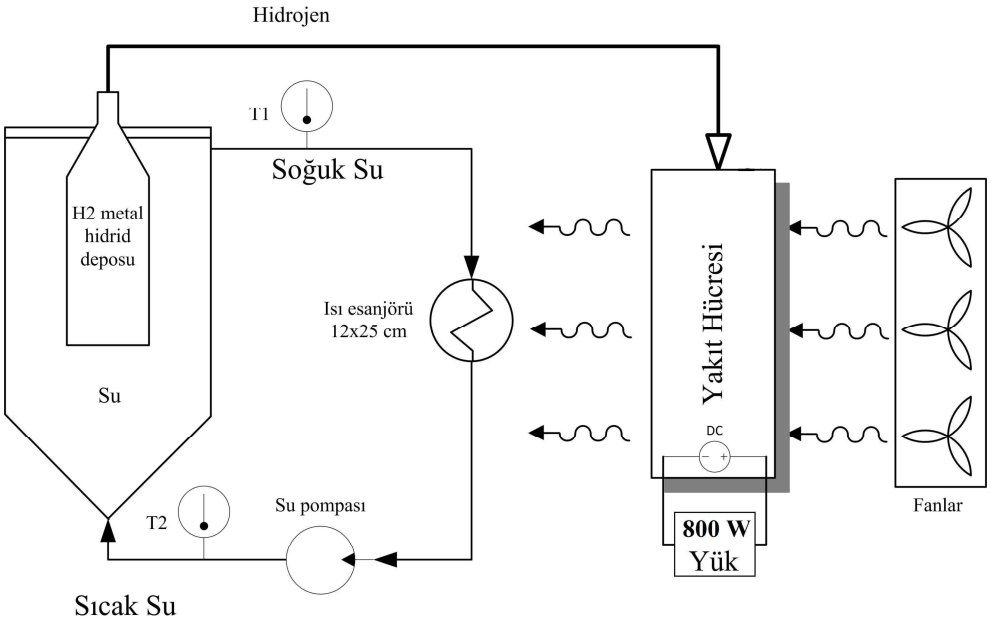
Enerji transferi yapan her sistemde kayıplar olduğu gibi, metal hidrid hidrojen saklama ortamlarında da emilen hidrojen ile salınabilen hidrojen miktarı arasında bir fark vardır. Emilen miktarın tamamı, bütünüyle salıverilememekte, bir miktar hidrojen depo içinde kalabilmektedir (Forde, 2009). Dolayısıyla salıverme esnasında metal hidrid saklama ortamının ısıtılması, salıverilen hidrojen miktarını arttıracağı için, metal hidrid deponun verimine pozitif yönde etki edecektir. Bu sayede belirli bir menzile ulaşmak için ihtiyaç duyulacak hidrojen deposunun hacmi ve ağırlığı düşürülmüş olacaktır. Keza, aynı hacim ve ağırlıkta, daha fazla hidrojenin salıverilmesi mümkün olacağı için aracın menzili artacaktır.

Bu çalışmada sabit mıknatıslı, fırçalı doğru akım bir elektrik motoruyla tahrik edilen, 3 tekerli, arkadan itişli, yakıt hücreli, elektrikli bir aracın, hidrojen saklama ortamının salıverme verimini arttırmak amaçlanmıştır. Blok şeması aşağıda verilen aracın,

polimer elektrolit membran tipli yakıt hücresi, hidrojen deposu olarak metal hidrid tüp grubu tarafından beslenmektedir.



Araçta kullanılan metal hidrid saklama ortamlarının salıverme verimini arttırmak amacıyla kapalı devre ısı transfer sistemi kurulmuştur. Kurulan sistemin blok şeması aşağıda verilmiştir. Normal çalışma sırasında bir grup fan, yakıt hücresinin soğutulması için, dış ortamdan emdiği havayı yakıt hücresine basmaktadır. Fanlar tarafından basılan soğuk hava, yakıt hücresinin ısısını almakta ve sıcak hava, yakıt hücresinden dış ortama aktarılmaktadır. Yapılan deneysel çalışmada, yakıt hücresine adapte edilen bir otomobil radyatörü ısı değiştirici olarak kullanılmıştır. Elektrikli araçta kullanılan metal hidrid tüplerden biri hidrojen ve sıvı giriş-çıkışına imkan veren kapalı bir kaba yerleştirilmiştir. Kurulan sistem sayesinde, yakıt hücresinden salınan ısının, radyatör vasıtasıyla alınarak metal hidrid tüpe kazandırılması amaçlanmıştır.



Yapılan deneyler sonucunda kurulan sistemin, salınan hidrojen miktarını kayda değer oranda arttırdığı görülmüştür. Yakıt hücresi, çıkışında 800W güç üretecek şekilde yüklenmiş; ilk olarak ısı transfer sistemiyle, daha sonra ısı transfer sistemi olmadan, aynı şartlarda doldurulmuş metal hidrid tüpe bağlanmıştır. Isı transfer sistemi ile çalışan metal hidrid tüp 61 dakika boyunca; ısı transfer sistemi olmadan çalışan tüp ise sadece 18 dakika yakıt hücresini ortalama 800 W güç üretecek şekilde besleyebilmiştir. Normal çalışmada 18 dakika sonra biten tüp, ısı transfer sistemi ile teste devam edildiğine 50 dakika boyunca yakıt hücresini aynı yükte (800W) besleyebilmiştir.

1. INTRODUCTION

1.1 Purpose of The Thesis

The main purpose of this study is to improve discharging efficiency of the metal hydride storage of an existing FCEV by closed-circuit heat transfer system to increase the total range of the vehicle.

The other purpose of this study is examining hydrogen production and especially storage methods for fuel cell electrical vehicles (FCEV) which are considered to decrease harmful effects of fossil fuels on environment caused by internal combustion vehicles and to supply future energy needs, efficiently, instead of fossil fuels.

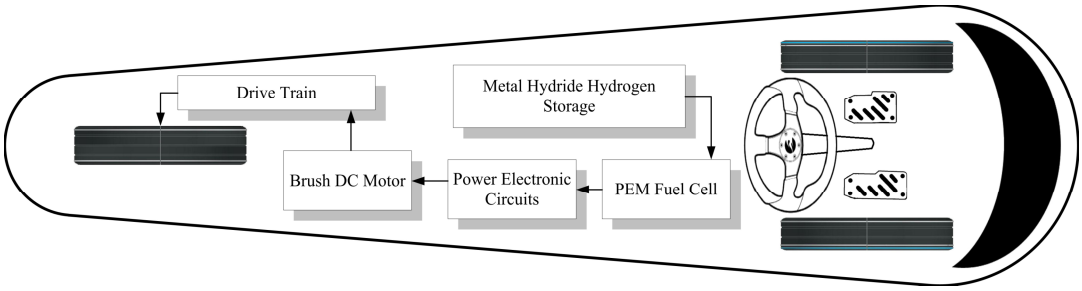


Figure 1.1 : Block scheme of Hydro-Bee, hydrogen fuel cell vehicle

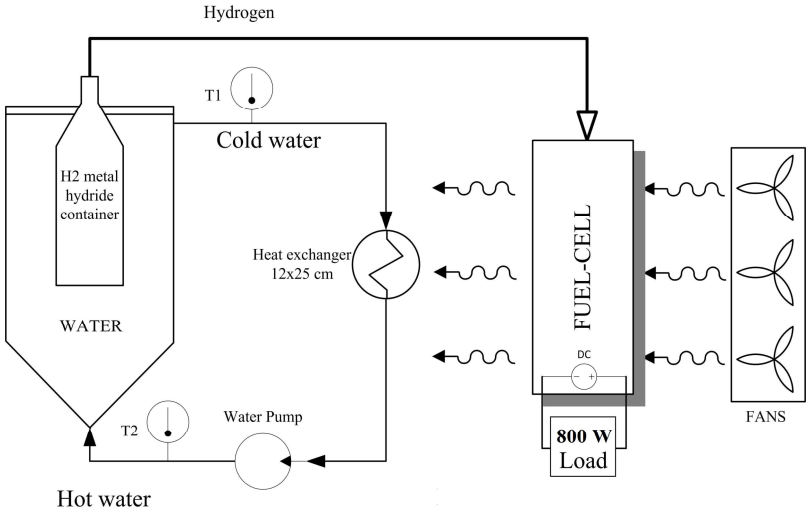


Figure 1.2 : Proposed, closed-circuit heat transfer system

1.2 Background

Transportation is one of the main needs of human being. People tend to move from somewhere to another depending on many objective or subjective causes, or they transfer objects from one point to another. In today's world, generally internal combustion vehicles (ICV) are used to provide transportation needs. Internal combustion vehicles consume fossil fuels and the ratio of transportation in fossil fuel usage has been increasing dramatically. Exhaust gases of ICVs contain environmentally harmful gases like CO_2, CO, NO_x, SO_x and unburned C_xH_x. These gases cause greenhouse effect and global warming.

Electrical and hybrid vehicles were developed to increase vehicle mileage efficiency, decrease fossil fuel usage and harmful gas emissions. Since electrical motor has any emissions and it runs at higher efficiency, electrical vehicles were produced. However, energy capacity per weight ratio of current batteries is low so hybrid vehicles, which have both electrical and internal combustion motor, were manufactured.

Hybrid vehicles have high efficiency and low emissions but since they still have some harmful emissions, researchers have focused on fuel cells, which were firstly developed by Sir William Grove in 1839. Fuel cells generate electrical energy without combustion and only produce water as an exhaust product. The fuel cell consumes oxygen from ambient air and hydrogen from hydrogen source. There are many kinds of fuel cells but especially polymer electrolyte fuel cells (PEFC) are well-matched with vehicle applications due to their short response times, quick start up, lower operating temperature and power performance.

Production and distribution systems of fossil fuels work properly. Fossil fuels refined in central plants and distributed to stations so people can easily get their needs from these stations. Development of zero-emission fuel cell vehicles mainly depends on hydrogen production, distribution and storage systems. As production is a quite complex process, it must be handled in central plants but also there must be a secure, feasible and effective hydrogen storage system for on-board usage.

Although, hydrogen can be stored in gas form at very high pressures or it can be stored in liquid form at very low temperatures, both of the system have safety problems because of high pressure or high temperature difference. Consequently

storing hydrogen in solid form seems as the most suitable way for vehicle applications. Hydrogen gas can be absorbed by solid substances ie. carbon materials or metal hydrides. Carbon materials have high atomic surface area but their storage capacity and reversible performance are poor.

There are three main types of metal hydrides; water reactive hydrides reacts with water and produce hydrogen, thermal reactive hydrides need heat to split up into hydrogen and base molecules. Both type of metal hydrides need central recycling to absorb hydrogen. The last type is rechargeable hydrides, which is accepted as the best option for vehicle applications due to the fact that they operate at lower pressure and temperature and they have sufficient storage capacity.

1.3 Hypothesis

Absorption and desorption processes of hydrogen by metal hydrides are thermo-chemical reactions. The metal hydride storage emits heat during absorption (exothermic) and needs heat (endothermic) during desorption. While metal hydride storage supplies hydrogen to a fuel cell, it starts to cool down. Cooling decreases the equilibrium pressure in the storage so desorption slows down until equilibrium pressure equals fuel cell pressure. At the end of the reaction, desorbed hydrogen is less than absorbed because of losses. Some amount of hydrogen can not be released from the storage, the ratio of released to stored hydrogen is defined as metal hydrides desorption efficiency. This study proposes a closed-circuit, heat transfer system to improve metal hydrides desorption efficiency. Proposed system transfers heat from the fuel cell to metal hydride storage. Thermal energy is collected by using of a radiator, which is fitted on fuel cell to take its removed heat. Heating increases the pressure of metal hydride storage and improves reaction kinetic as a result, more hydrogen can be desorbed and desorption efficiency increases.

$$M + xH_2 \rightarrow MH_x + Heat \qquad \text{Absorption Reaction} \qquad \textbf{(1.1)}$$

$$MH_x + Heat \rightarrow M + xH_2 \qquad \text{Desorption Reaction} \qquad \textbf{(1.2)}$$

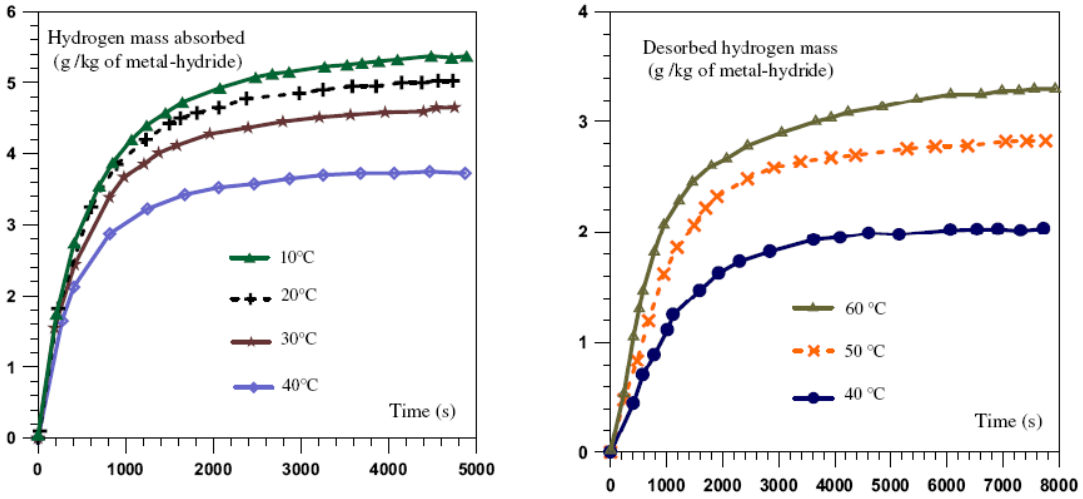


Figure 1.3 : Absorption and desorption charecteristics of metal hydrides

When a fuel cell electrical vehicle is considered, there are many heat sources such as fuel cell, power electronic circuits, breaks or surface of the car. At this experimental study, only fuel cell's removed heat, which is taken by cell's cooling system, is used to heat up the metal hydride storage.

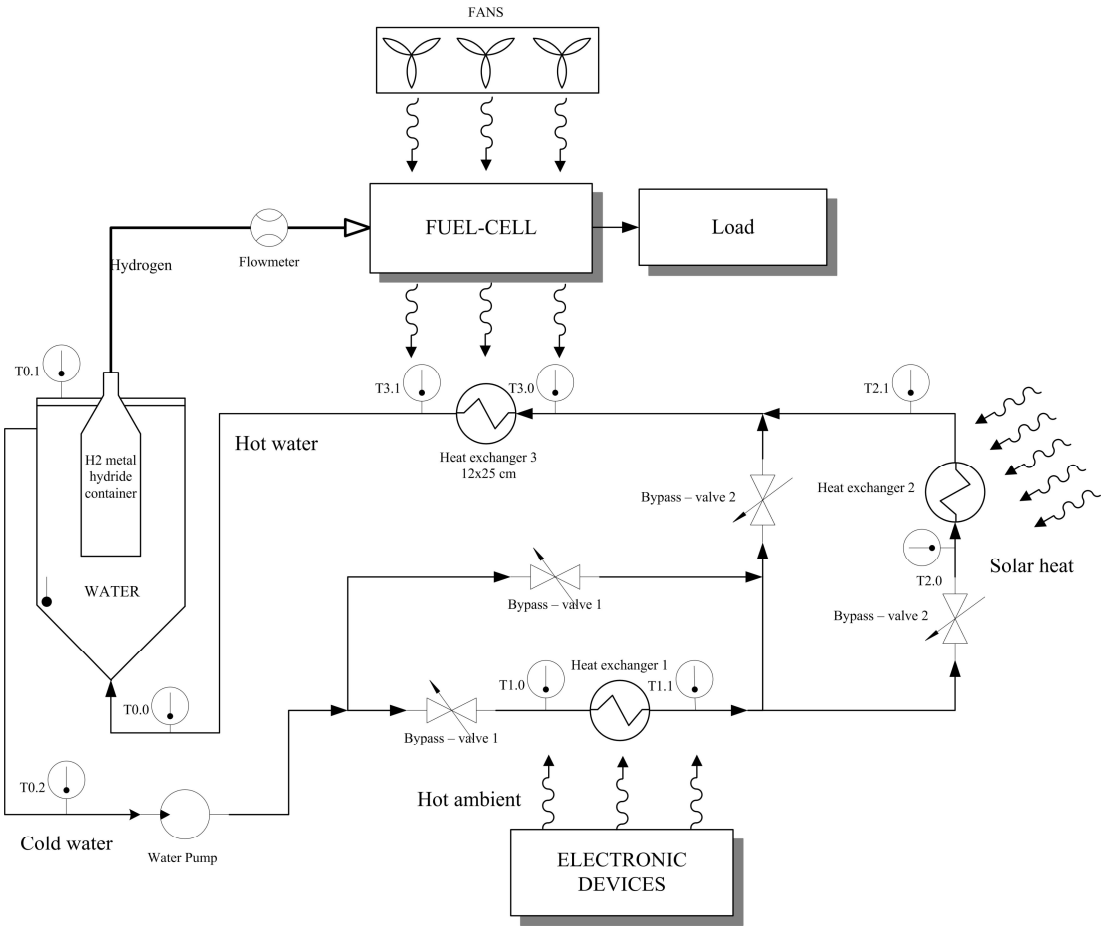


Figure 1.4 : An extended general diagram of heat sources to heat up MH storage.

2. ELECTRIC VEHICLES

2.1 Effects of Conventional Vehicles on Earth

Combustion of carbon-hydrogen based fuels produces pollutant gases called greenhouse gases. CO_2 is one of these gases which mainly causes global warming. Combustion is a typical process, which is applied in different areas for example, transportation or industry. As seen on graphic, the ratio of transportation systems in fossil fuel usage is 32%, so many pollutants such as CO_2, NO_x, CO, SO_x and not burned hydrocarbons are emitted by ICV (Ehsani, 2010).

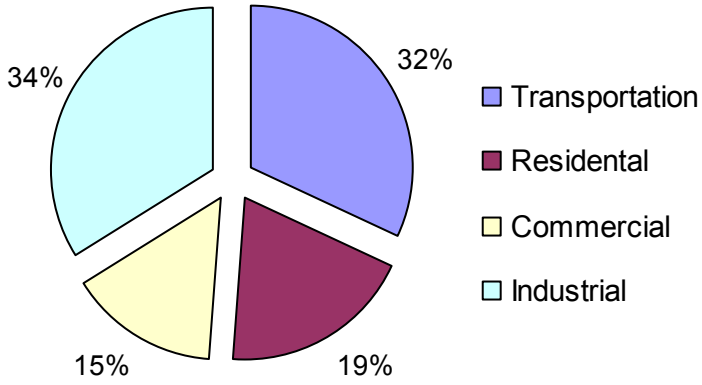


Figure 2.1 : Distribution of Fossil Fuel Usage

If the ratio of transportation is analyzed, it can be seen from Figure 2.2 that both the ratio of transportation and overall emissions have been increasing. The effect of emissions causes global temperature increase. Figure 2.3 reveals that except a few years, global temperature have been increasing. This is a proof of global temperature goes parallel with (Ehsani, 2010).

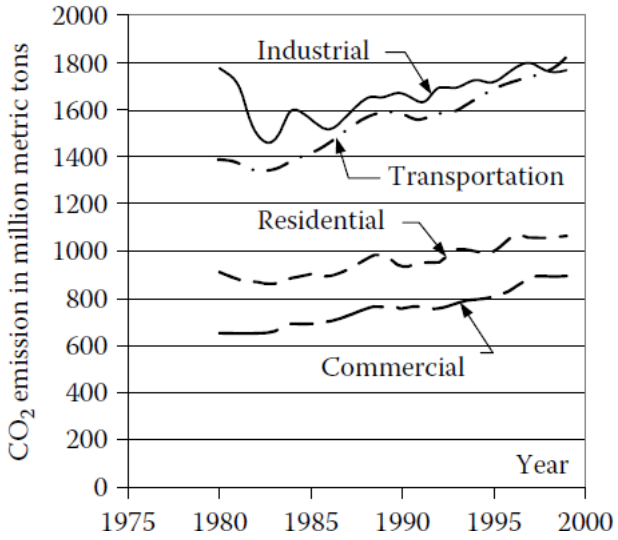


Figure 2.2 : Trend of CO_2 emission by years

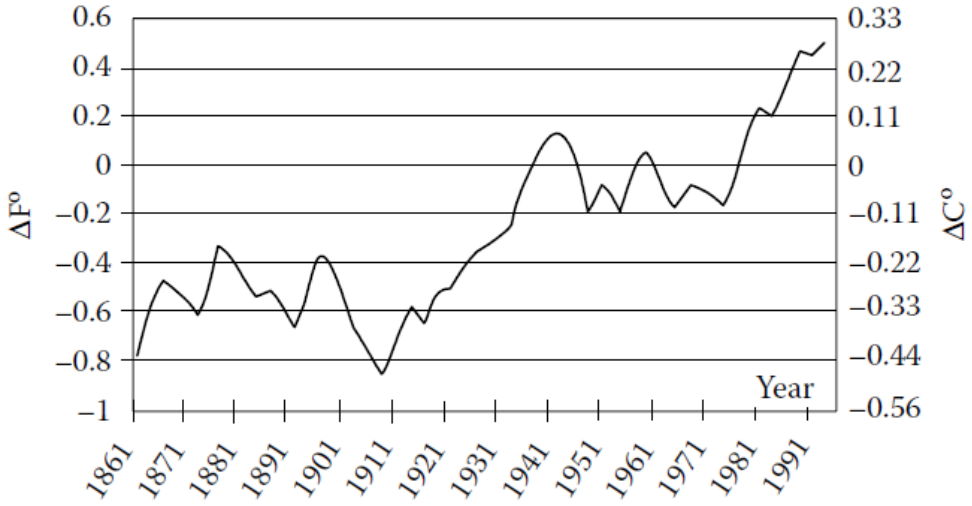


Figure 2.3 : Global temperature trend (EPA)

Shortage of fossil fuels is another problem besides their negative effect on environment. Middle East has the richest petroleum reserves, the second one is South America which only has 1/7 of Middle East. According to US Geological Survey in 2000, current reserve is 142 billion tons while undiscovered potential reserve is 98,3 billion tons. When daily consumption is taken into account, shortage of petroleum becomes an essential problem of the world (Ehsani, 2010).

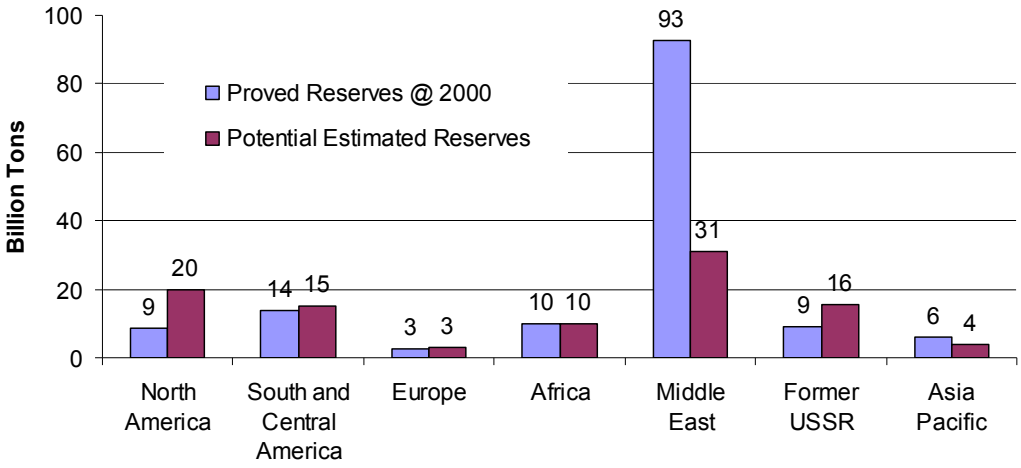


Figure 2.4 : Proved and estimated potential petroleum reserves

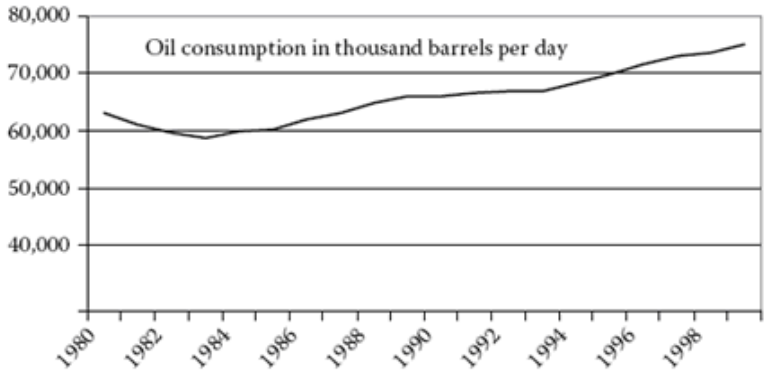


Figure 2.5 : Trend of daily oil consumption by years

The ratio of transportation in oil consumption is very important. Figure 2.6 reveals that the increase of oil consumption by years. According to Ehsani (2010) oil consumption in transportation will reach up to 60% in 2020 while its current ratio is about 45%.

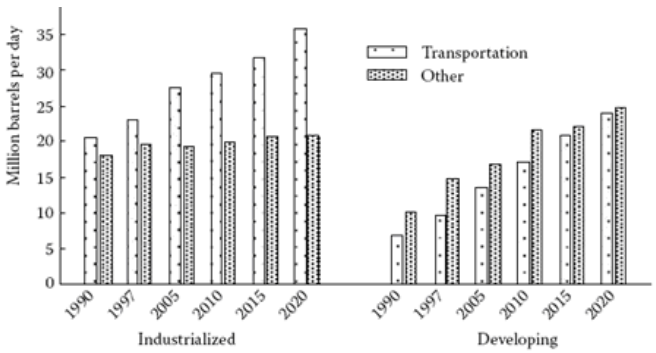


Figure 2.6 : Oil consumption of the world, transportation and others

2.2 General Information About Internal Combustion Vehicles

General concept of an automobile is given in Figure 2.7. There is an internal combustion engine, which generates mechanical power. There is either a clutch for manual transmission or a torque converter for automatic transmission to transfer power from motor to gearbox. The gearbox sets speed/torque ratio for desired load point. Then, final drive and differential decline speed and distribute power for each wheels.

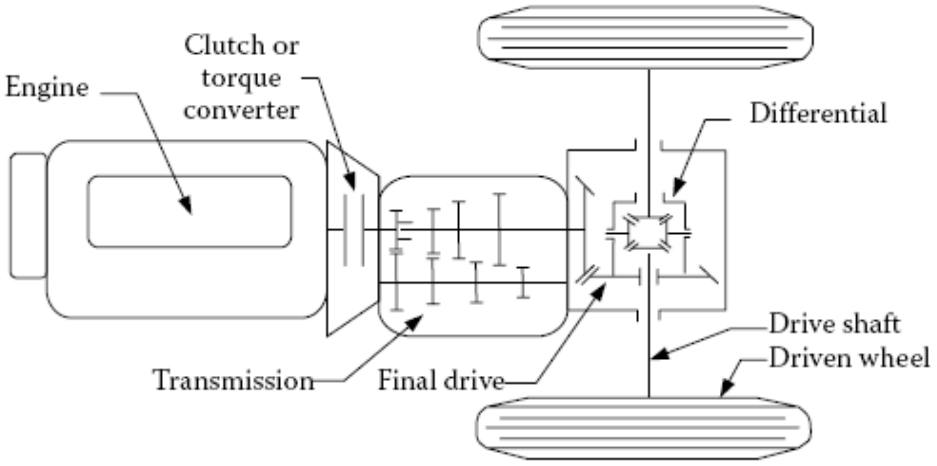


Figure 2.7 : General overview of an internal combustion engine vehicle

Internal combustion engine is the main part of a vehicle as it generates required mechanical power for the load. A four-stroke internal combustion engine consists of cylinder, piston, crank, inlet-exhaust manifold and inlet-exhaust valve that are given in Figure 2.8. A four-stroke internal combustion engine works in a routine cycle, which has four steps. The first step is induction in which air/fuel mixture enters cylinder. The second step is compression in which air/fuel mixture is compressed to get ready to ignition. Thirdly, the temperature and pressure of combusted mixture increase and the product gases expand in expansion step. Lastly, in exhaust step outlet valve is opened and product gases are removed.

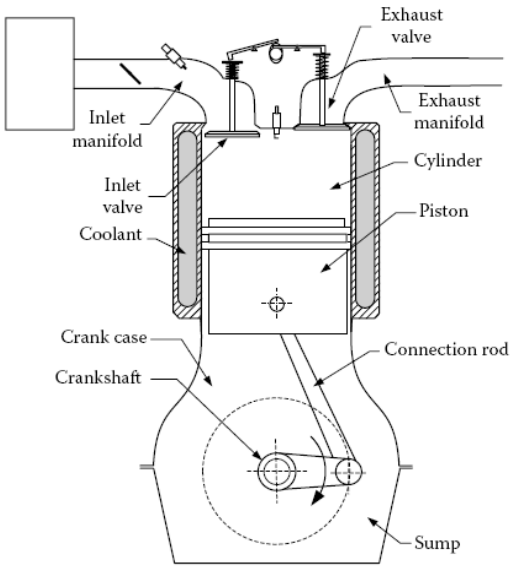


Figure 2.8 : Main parts of an internal combustion motor

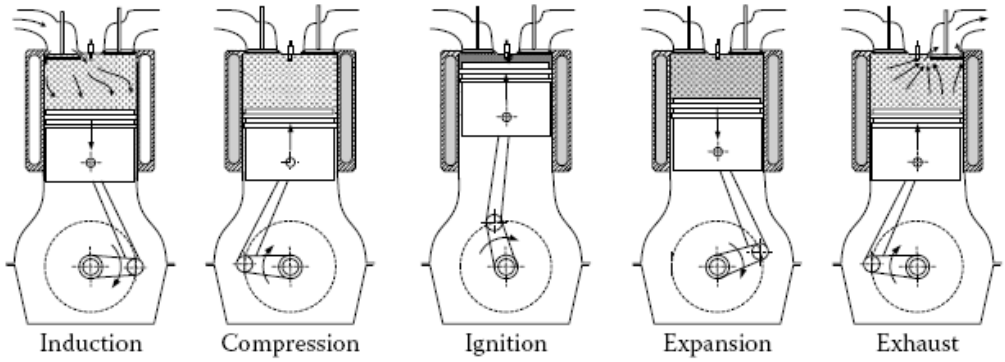


Figure 2.9 : Four steps of routine internal combustion motor cycle

2.3 History of Electric Vehicles

The first attempts to make electric car and related developments were made in 1881 in France and Great Britain. EV cars did not take the publics attention since they had low range and speed. In 1876, Otto introduced the internal combustion engine, after that the competition started between EVs and Otto's gasoline engines. Especially in Europe, roads were paved, consequently the range of vehicles was supposed to be long. Since the energy capacity of EVs were not powerful enough to run the same vehicle at the same range like ICVs, people preferred ICVs to EVs. In 1897, a French man, M.A. Darracq, developed regenerative breaking which enabled to convert kinetic energy to electrical energy (Ehsani, 2010). This development also helped to

increase EV vehicles' range but still it was not enough to compete with gasoline vehicles. Another French man, whose name was Camille Jenatzy, designed an electric car and reached 100 km/h (68 mph) speed that was the world record broken by a racing car named " La Jamais Contente".

Electric cars are preferred because they do not have vibration, bad smell and noise while gasoline engines have. Moreover, transmission is another main problem of gasoline cars; on the other hand, electric cars do not need any transmission because power electronic circuits can change the speed and torque of an electrical motor. The base of power electronic circuits is transistor, which was invented in 1945 in Bell Laboratories. This invention made a real revolution for electronic equipments.

Despite having technical advantages, electric cars lost their popularity because cities were getting bigger and oil costs were decreasing. The range of electric cars was short, so longer-range became a serious requirement but it meant better electrical equipment and higher-cost. In addition, oil prices were decreasing, the new crude oil refineries started to run and Charles Kettering invented the electrical start-up mechanism, which eliminated hand crank. Henry Ford started a serial production and typical gasoline car price became 500-1000 $ while equivalent electric car was being sold for 1750 $.

In conclusion, because of being durable and feasible, gasoline car became popular and commercial. The crude oil was cheap and two main problems of gasoline engine were solved. On the other hand, it did not take too long that world beware of exhaust gas emissions and their harms on environment. Moreover, fossil fuels were limited energy sources. Any other clean, renewable and environment friendly technologies had to be developed so scientists, again, have started to work on electric vehicles.

2.4 Electric and Hybrid Vehicles

Since internal combustion vehicles (ICV) have serious problems, electric vehicles (EV) and hybrid electric vehicles (HEV) are considered as the solution. For example IC motors do not run at optimum efficiency point, they emit greenhouse gases, their breaking kinetic energy is lost and they run at lower efficiency for run/stop working due to transmission losses. EVs have some advantages over ICVs such as zero-emission and higher motor efficiency. Despite being more advantageous than ICVs

EVs suffer from lower range because of lower battery capacities. A typical fuel tank's energy capacity is 50 times greater and 100 times lighter than a typical lead-acid battery (Demirel, 1998). HEVs have both types of internal combustion and electric motor to use positive sides of each motor type. However, they are not zero-emission vehicles.

Block scheme of basic EV is given in Figure 2.10. Energy storage is a group of battery instead of fuel tank and an electric motor takes place of internal combustion motor. Figure 2.10 reveals different types of EVs. For example, the first type, the electric motor can be on the same shaft with wheels. Secondly, there can be two electric motors coupled with fix gears to front wheels. Third option is directly coupled electric motors to wheels. The last option is hub motors mean the electric motor and wheel is the same object. The fixed side is stator of electric motor while the rotating side is used as a wheel. ,

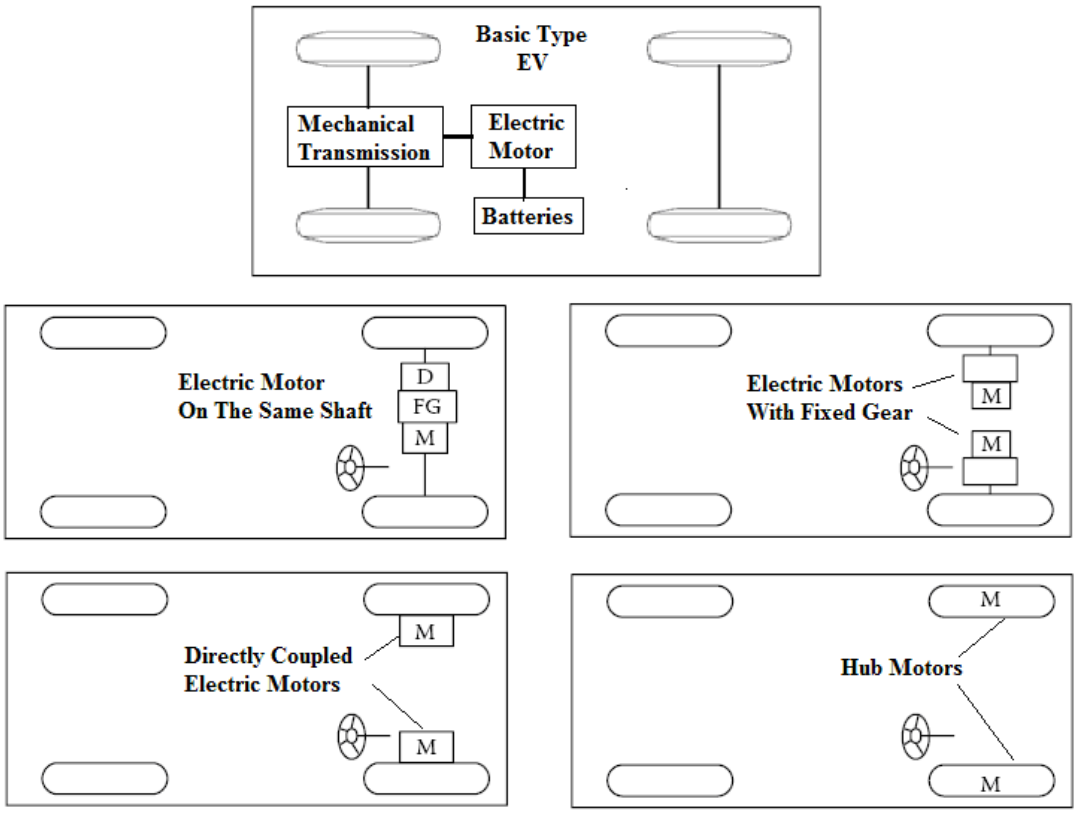


Figure 2.10 : Different types of EVs

A hybrid vehicle has two or more power converter. As mentioned above, HEVs have advantages of both ICVs and EVs because they include an electric motor and internal combustion motor. The range of HEVs is high because of IC engine and their energy

efficiency (mileage) is high because of electrical motor and regenerative breaking. HEVs emit a few pollutant gases and they are convenient for run/stop daily operating conditions. Being suitable for variable load characteristic makes HEVs efficient. The load characteristics can be divided into steady state load and instantaneous load. IC motor is more suitable to drive constant and heavy loads, as everybody knows fuel consumption is low for long ways. So in HEVs electrical motor is used for instantaneous and light loads.

There are three main types of HEVs as shown in Figure 2.11. The first one is electrically coupled series hybrid. The fuel and IC motor are operated at maximum efficiency point and generator supplies power for batteries. The second type is parallel hybrid. Both electrical motor and IC motor supply the power. The third one is series-parallel hybrid, which takes advantage of both series and parallel hybrid but it is not as cheap as series or parallel type.

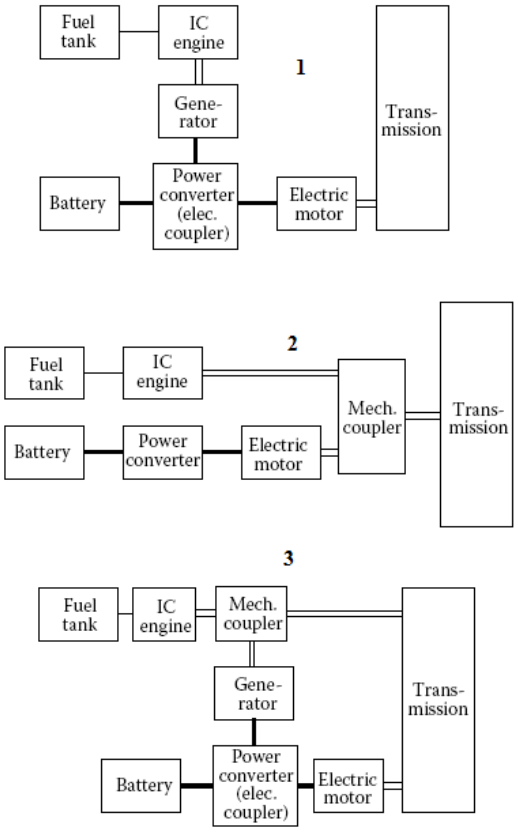


Figure 2.11 : Hybrid vehicle types

2.5 Benefits of Electric Vehicles

Conventional cars, which are powered by internal combustion engine, have been replacing with new, eco-friendly electric drives. To decrease emission of pollutant gases and energy consumption of vehicle electric motors are seemed as the best solution. It is also possible to divide electric vehicles into two groups: Fuel Cell Powered and Battery Powered.

During fuel cell operation, the fuel cell emits water and heat contrary to common combustion engines they do not emits pollutant gases such as carbon dioxide or carbon monoxide. The main advantage of fuel cell is energy source consist of hydrogen and atmosphere based oxygen. It is estimated that by replacing ICVs with EVs, emission of non-methane organic gases will be reduced 98% and nitrogen oxide gases will be reduced 92% and the most important result CO_2 emissions will be reduced 99% .

Electrical vehicles (EV) are more efficient than conventional engine vehicles. The input energy of a battery powered electrical vehicle is charging power. On the other hand, energy input of an ICV is filled fuel in the tank. The output energy of both vehicles is the energy on tires so when input/output ratio of both vehicles is compared, EV efficiency is 46% while ICV equals 18%.

Another advantage of EVs is being more reliable than ICVs since they don't have too much moving equipment. Transmission is a critical problem of ICVs. There are a lot of gear mechanisms; chains, belts, pistons and engine oils are needed to be able to operate the vehicle in a determined position. On the other hand, EVs do not require extra mechanisms and oils because a power electronic circuit can change the speed-torque point of the electric motor and also there is an opportunity to specify the nominal speed of the motor by changing poles/windings at manufacturing site.

Noise is a serious harmful pollution, which affects cardiovascular and psycho physiological systems, it decreases performance at work or at school and also it causes sleep disorder. Especially traffic noise is an essential harming issue. According to the researches every third person is badly get harmed by traffic noise and every fifth person is subjected to higher decibel sound levels at nights. A person is exposed to about 80-85 dB at city traffic inside the car while normal talk is 70 dB and 90-95 dB is accepted value, which causes hearing loss. ICV manufacturers

design many isolation solutions to block the sound of motor to pass inside the car. These are also additional equipments, which also increase cost and consist of generally petroleum made products. Since electric motors are silent machines and they do not include extra gear mechanisms, which also create noise, EVs will be beneficial for human health both inside and outside of the car.

In conclusion, being zero-emission (zero-pollutant) and higher-efficiency and working quiet make EVs the vehicle of future. They do not consume fossil fuel, they work quieter and their efficiency is very high. These are very important parameters for a vehicle when compared with existing ICVs. The question is the source of energy. Some alternatives, which may decrease pollutant gas emission and increase efficiency, will be investigated in next chapters.

3. ALTERNATIVE ENERGY SOURCES FOR VEHICLES

3.1 Solar Energy

The first solar cell was introduced in 1954 in ”Bell Telephone” laboratory. After that, they were used in Vanguard 1 space vehicle and their good performance attracted researchers interest on solar cells (Demirel, 1991). Solar cells, also called Photovolatics (PV), convert sun light energy directly to electrical energy. Main advantages of PV systems are; typical efficiency is high, %14, which is 14 times of thermo-electrical converter system; their life is too long, output power/weight ratios are high and the most important they are one of the zero-emission energy sources. Despite having many advantages and being useable and common, serious technical improvements are required for PV systems to be feasible for vehicle applications. Firstly, the cost of solar cells is still very expensive. Secondly, they need an energy storage, like batteries. Thirdly, required surface is much more for a typical four wheel automobile. Fourthly, they are too sensible for weather conditions, sometimes higher temperatures can harm solar cells. On the other hand, the usage of photo-volatics in stationary applications has been increasing regularly, especially in Europe. Piebalgs (2009) reported that existing photovolatic capacity has reached and even passed the targets which were determined by White Paper in 1997. Now, the capacity of existing photovoltaics is 16 000 MW whereas the White Paper 2010 target was 3 000 MW.

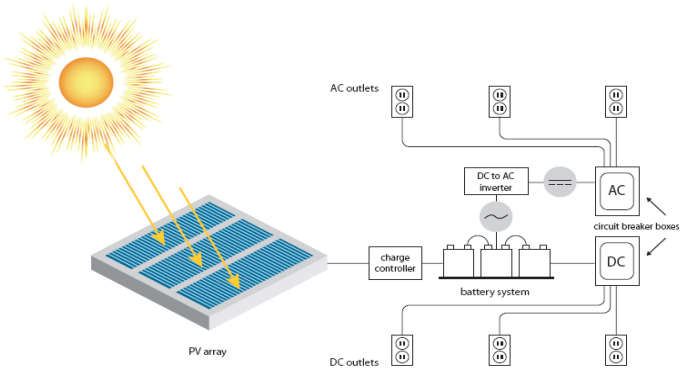


Figure 3.1 : Block scheme of solar plants

Solar energy constant in other words the description of power density created by the sun and given to the atmosphere is 1.373 kW/m^2. About 0.3 kW part of it is absorbed by some layers of atmosphere and as a result 1 kW/m^2 is the maximum residual value (Rashid, 2001). The role of photovolatics is converting this energy to another form, electrical energy. The main part of photovoltaics is solar cell. Solar cell includes p-n junction like a diode. Thickness is about 0.2-0.3mm and made up from monocrystaline or polycrystalline silicon wafer, which has two different electrical characteristic. Sun lights include photons and photons hit solarcell junctions and gets electron. This electron runs from out-circuit and reaches other side of junction so this action creates electrical current.

There is an opposite relation between PVs current and voltage. If load equals zero like short circuit, diode voltage will be zero, too. When load resistance increases, current will be divided to two paths, diode and load current. When load resistance reaches open circuit condition, whole current flows to diode. Below equation reveals the relationship between current and voltage.

$$I = I_{ph} - I_0 \cdot \left(e^{\frac{q.V}{k.T}} - 1 \right) = I_{ph} - I_d \qquad \textbf{(3.1)}$$

q : electron charge, k : Boltzman constant

I_{ph} : Photocurrent

I_0 : Reverse current, I_d : Diode current, T : operating temperature (Kelvin)

There are three main types of semiconductor materials which are feasible to be used in solar cell production.

- Monocrystalline Si cells
- Polycrystaline Si cells
- Amorphous Si cells

Open-circuit voltage and short-circuit current are the two main points of every type of solar cells. The typical open-circuit voltage is 0,6-0,7 V/cm^2 and typical short-circuit current is 20-40 mA/cm^2. The relation of I_{sc} with illumination is proportional but at the same time the relation of Voc with illumination is logarithmic.

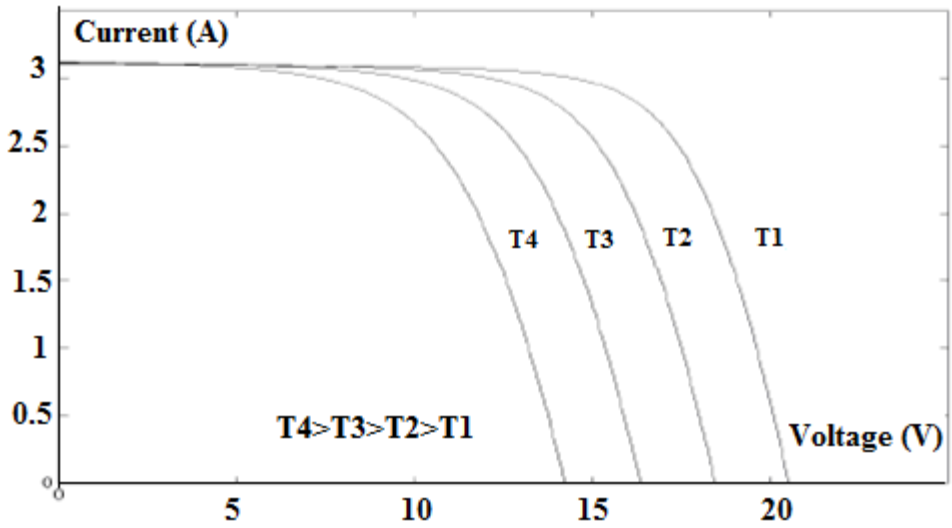


Figure 3.2 : The effect of temperature on current-voltage characteristic of PVs

Below Figure shows that if temperature increases open circuit voltage decreases. So operating temperature is an important factor for photovoltaics. Typical solar cell temperature is 20-40 ^{o}C bigger than ambient (Demirel, 1991). Battery selection is another key point for PV applications.

There are some challenges of photovoltaics for electrical vehicles for example; too large surface area is needed to run a basic car at moderate performance in average range. Secondly, as mentioned above, outside weather conditions have great effect on their performance since photovoltaics convert solar energy. Another disadvantage is being very expensive and having long pay-back time. And there are too many technical coefficients, which must be well analyzed before application, such as; low current on charging and discharging, deep discharge, irregular discharge.

3.2 Biomass

Biofuels are a wide range of fuels which are in some way derived from biomass. The term covers solid biomass, liquid fuels and various biogases (Demirbas, 2009). Biofuels are gaining increased public and scientific attention, driven by factors such as oil price spikes, the need for increased energy security, and concern over greenhouse gas emissions from fossil fuels.

Bioethanol is an alcohol made by fermenting the sugar components of plant materials and it is made mostly from sugar and starch crops. With advanced technology being developed, cellulosic biomass, such as trees and grasses, are also used as feed stocks

for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil.

Biodiesel is the most common biofuel in Europe (Bringezu, 2009). It is produced from vegetable oils, animal fats or recycled greases. Biodiesel can be used as a fuel for vehicles in its pure form (B100), but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. In the pure form is the lowest emission diesel fuel. Although liquefied petroleum gas and hydrogen have cleaner combustion, they are used to fuel much less efficient petrol engines and are not as widely available.

Biodiesel can be used in any diesel engine when mixed with mineral diesel. In some countries manufacturers cover their diesel engines under warranty for B100 use, although Volkswagen of Germany, for example, asks drivers to check by telephone with the VW environmental services department before switching to B100. B100 may become more viscous at lower temperatures, depending on the feedstock used. In most cases, biodiesel is compatible with diesel engines from 1994 onwards, which use 'Viton' (by DuPont) synthetic rubber in their mechanical fuel injection systems.

Electronically controlled 'common rail' and 'unit injector' type systems from the late 1990s onwards may only use biodiesel blended with conventional diesel fuel. These engines have finely metered and atomized multi-stage injection systems that are very sensitive to the viscosity of the fuel. Many current generation diesel engines are made so that they can run on B100 without altering the engine itself, although this depends on the fuel rail design. Since biodiesel is an effective solvent and cleans residues deposited by mineral diesel, engine filters may need to be replaced more often, as the biofuel dissolves old deposits in the fuel tank and pipes. It also effectively cleans the engine combustion chamber of carbon deposits, helping to maintain efficiency. In many European countries, a 5% biodiesel blend is widely used and is available at thousands of gas stations. Biodiesel is also an oxygenated fuel, meaning that it contains a reduced amount of carbon and higher hydrogen and oxygen content than fossil diesel. This improves the combustion of fossil diesel and reduces the particulate emissions from un-burnt carbon.

Biodiesel is also safe to handle and transport because it is as biodegradable as sugar, 10 times less toxic than table salt, and has a high flash point of about (148º C)

compared to petroleum diesel fuel, which has a flash point of (52º C) (Thurmond, 2007).

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Biogas is produced by anaerobic digestion or fermentation of biodegradable materials such as biomass, manures, sewage, municipal waste, green waste, and plant material and energy crops. This type of biogas comprises primarily methane and carbon dioxide (NNFCC, 2009).

The gases methane, hydrogen and carbon monoxide can be combusted or oxidized with oxygen. This energy release allows biogas to be used as a fuel. It can be used in modern waste management facilities where it can be used for electricity production on sewage works, in a CHP gas engine, where the waste heat from the engine is conveniently used for heating the digester, cooking, space heating, water heating and process heating. If compressed, it can replace compressed natural gas for use in vehicles, where it can fuel an internal combustion engine or fuel cells and is a much more effective displacer of carbon dioxide than the normal use in on-site CHP plants. Biogas is a renewable fuel, so it qualifies for renewable energy subsidies in some parts of the world (Baldwin, 2008).

3.3 Hydrogen Energy

The hydrogen is one of the best energy sources for many reasons; it does not include carbon so does not produces greenhouse gases, it has unlimited natural source such as water, its energy per volume ratio is very high and there are many producing and storage opportunities (Jain, 2009).

Firstly, CO_2 emission is very low when compared with other energy sources. Annual mean temperature of the world is regularly increasing due to CO_2 emissions. Weather conditions and seasonal temperatures are changing surprisingly as a result agricultural and zoological lives are going bad. Product of fossil fuels; CO_2, CO, SO_2, are harmful for the earth. Recent years, there are many regulations and standards have been being published and people have realized that CO_2 emission is harmful and it must be declined. Additionally, CO_2 footprint and energy efficiency class have been started to calculate for all energy-consuming equipments. The

shortage of conventional energy sources forced people to find new energy sources and people have to use existing energy sources more efficiently..

Secondly, hydrogen has very wide range of source. When calculated elemental density of the universe, hydrogen gets the first place with 75% mass ratio. Likewise, 70% of the world's surface is covered with oceans and water consists of hydrogen and oxygen atoms. Moreover, fossil fuels and foods are chemical compounds of hydrogen and carbon. As a result, hydrogen can be produced by water, fossil fuels or biomass.

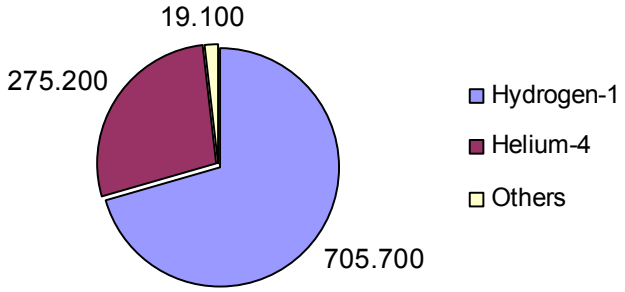


Figure 3.3 : Mass ratio of universe

The issue is solving energy requirement of people as efficient as possible. The cost, weight, volume must be minimum while efficiency and the amount of energy must be maximum. When compared with other traditional energy sources, it can be seen that hydrogen has the best energy per volume ratio. It equals three times of petroleum or five times of coal. Energy capacity at constant weight is shown on Figure 3.4 (Selvam, 1986). The same energy could be obtained from hydrogen at lower weight and volume rather than fossil fuels. Consequently, production, transportation and operating costs decrease seriously.

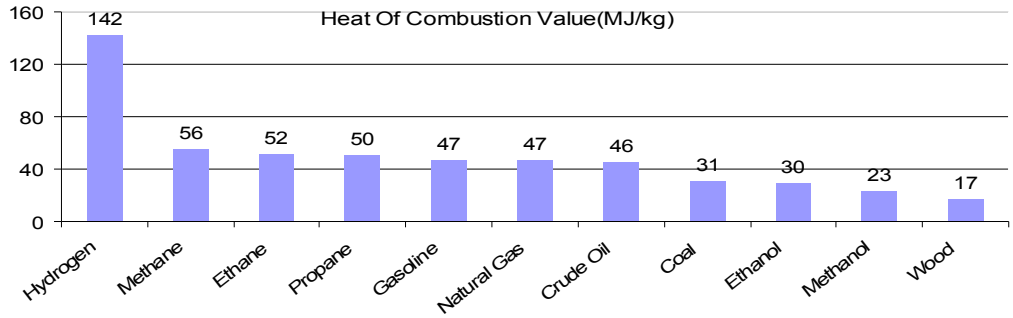


Figure 3.4 : Combustion heat value of different gases

Finally, there are many storage possibilities for hydrogen such as gas, liquid or solid systems. Hydrogen could be stored in gas form at very high pressures ie. 350 to 700 bar. Another way to stock hydrogen is keep it in liquid condition in croyogenic tanks. On the other hand, the common and industrialized method is solid systems. Metal hydrides and carbon materials are the most popular hydrogen capture opportunities. Detailed information will be given proceeding chapters.

4. FUEL CELLS

A fuel cell is the space in which electricity produced without combustion. The difference between the fuel cell and the battery is that fuel cells are infinite, while batteries are finite because, fuel cells are energy converters but batteries are energy sources. Generally, pure hydrogen or other hydrogen containing compounds such as hydrocarbons, ammonia are used as a fuel for these cells (Ehsani, 2010).

There are three main parts of a fuel cell: Anode, Cathode and Electrolyte. Typically, hydrogen molecules are inserted in the anode and it separates hydrogen ions and free electrons. Hydrogen ions go through the cathode and meet oxygen molecules. At the same time, free electrons move from anode to cathode by different path called electrical current. At cathode, chemical reaction is completed. Hydrogen atoms, oxygen molecules and free electrons combined together and water is made. (EG&G Technical Services Inc., 2004).

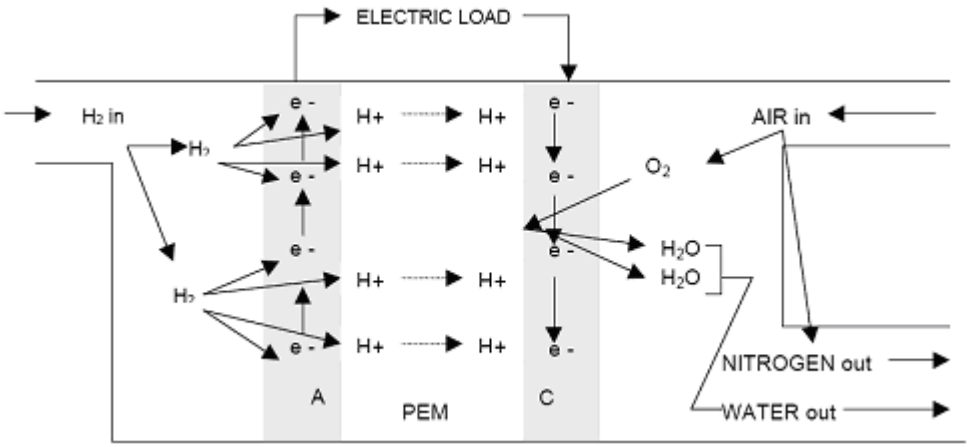


Figure 4.1 : Fuel cell operation

$2H_2 \rightarrow 4H^+ + 4e^-$ …Anode Reaction **(4.1)**

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ …Cathode Reaction **(4.2)**

$2H_2 + O_2 \rightarrow 2H_2O + Electricity + Heat$ …Cell Reaction **(4.3)**

Sir William Grove, who was called “Father of The Fuel Cell”, discovered fundamentals of fuel cell in Britain in 1839. He found the idea of producing electricity by using oxidation and reduction reactions but, later, fuel cells hadn’t been being used over a hundred years except space projects like the Apollo or Gemini. The reason is simple; material costs were very expensive. However, automotive industry has been using fuel cells since mid 1960’s (Ehsani, 2010).

4.1 Fuel Cell Performance

The rate of change of Gibbs free energy constant defines optimum electrical work under constant temperature and pressure conditions.

$$W_{el} = \Delta G = -n.F.E \tag{4.4}$$

n : is the electron number in reaction, F is faraday constant, E is optimum potential of the cell

Below formula also calculates The Gibbs Free Energy Constant

$$\Delta G = \Delta H - T.\Delta S \tag{4.5}$$

ΔH is enthalpy change and ΔS is entropy change

$T.\Delta S$ is waste or useless energy due to varying entropy. If reaction generates heat this means negative entropy, if reaction needs heat this means positive entropy.

Efficiency of the fuel cell is

$$\eta = \frac{BeneficialEnergy}{\Delta H} \tag{4.6}$$

$$\eta_{ideal} = \frac{\Delta G}{\Delta H} \tag{4.7}$$

Basic reaction :

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O + Electrical.Energy + Heat \tag{4.8}$$

At normal conditions, 25 ^{o}C and 1 atm, $\Delta_H = 285{,}8$ kJ/mole and $\Delta_G = 237{,}1$ kJ/mole

So ideal efficiency

$\eta_{ideal} = 0{,}83$

$$\eta = \frac{BeneficialEnergy}{\Delta H} = \frac{BeneficialEnergy}{\left(\frac{\Delta G}{0{,}83}\right)} = \frac{V_{real} x I_{real}}{\left(\frac{V_{ideal} x I_{real}}{0{,}83}\right)} = \frac{0{,}83 x V_{real}}{E_{ideal}} \quad \textbf{(4.9)}$$

If hydrogen and oxygen accepted 100% pure and pressure is 1 atm and temperature is 25 ^{o}C, ideal potential E equals 1.229 V for liquid form and 1.18 for gas form of output water. So, equation becomes:

$$\eta = 0{,}675 x V_{real(cell)} \quad \textbf{(4.10)}$$

There is a difference between ideal potential because different conditions of water results in gibbs free energy change due to vaporization. The effect of temperature on ideal potential is seen on below graphic (EG&G Technical Services Inc., 2004).

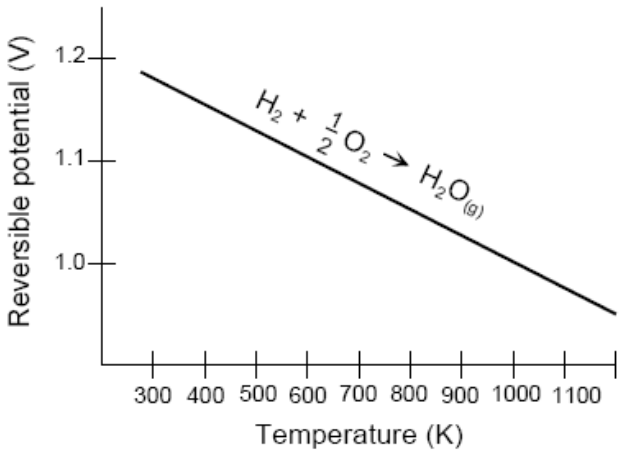


Figure 4.2 : The effect of temperature on fuel cell

The cause of difference between ideal and real is non-reversible losses such as reaction rate losses, ohmic losses due to electrolyte resistance to ion flow and electrode resistance to electron and the last one gas transport losses.

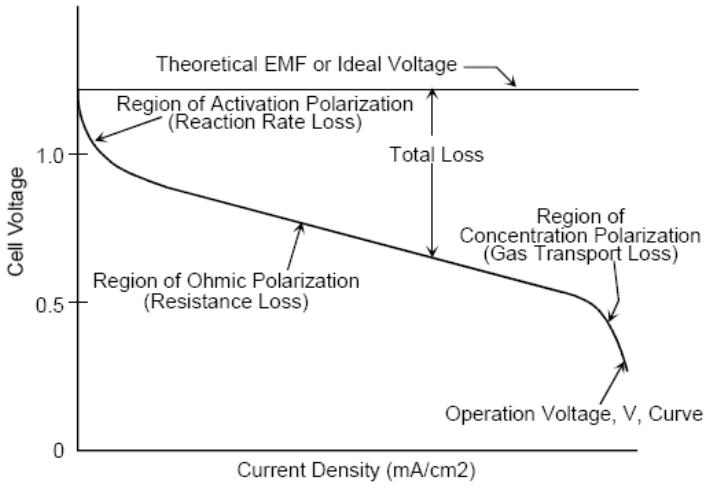


Figure 4.3 : Loss division for fuel cell

Current density is an important coefficient, which affects fuel cell performance seriously. At the beginning of the reaction, start-up current flows but reaction speed is low and voltage decreases. During normal operation, electrode and electrolyte resistances cause voltage drop. At high current ratios, necessary reactant can not pass cathode side as a result voltage decreases. Below Figure shows the relation of voltage-current and power-current. Minimum power means maximum voltage and lower current density. On the other hand, maximum power means minimum voltage and minimum cell efficiency so optimization must be handled.

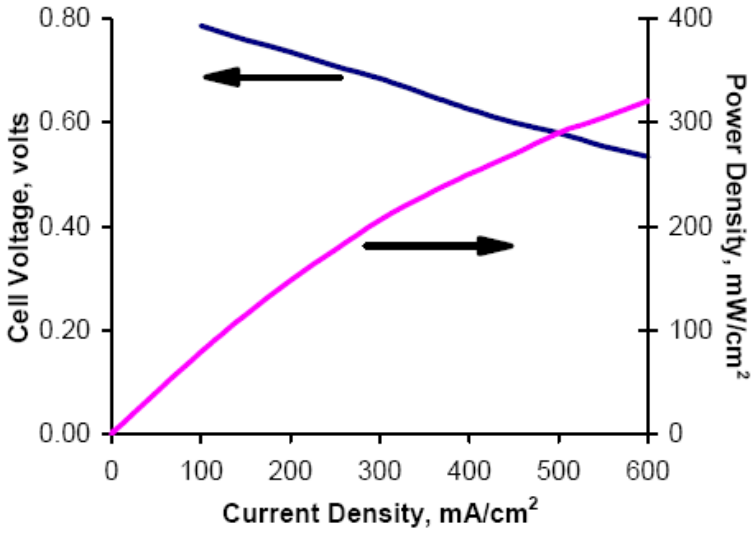


Figure 4.4 : Performance of Fuel Cell

Temperature is another critical factor, which determines cell performance with pressure. As H_2 and O_2 reaction is exothermic, any increase in temperature will

decrease (0.84mV/^{o}C) potential of the fuel cell. Furthermore, positive pressure change improves performance and rises up potential voltage. Nevertheless, temperature has other effects. For example, higher temperature enhances electrode reactions. Secondly, on the contrary to normal conductive materials, any increase in temperature, declines ohmic resistance and promotes reaction.

4.2 Fuel Cell Types

4.2.1 Alkaline fuel cells (AFC)

There are two kinds of KOH electrolyte concentration one of them is about %85 and the other one is about %40 percent while higher one operating temperature is 250 ^{o}C and lower one is less than 120 ^{o}C. Only hydrogen is usable as a fuel supply because for example CO_2 is harmful as it tends to react with KOH to create K_2CO_3.

Development of AFC had started in 1960, which was a famous project, The Apollo Space Vehicle. The AFC was used to supply electrical energy for Apollo. Despite being successful, the AFC had some difficulties especially CO_2 sensivity. There are two important advantages of the AFC: many kinds of electro-catalysts are usable and its electro kinetic is very active so these make the AFC's performance admirable. On the other hand, the AFC requires high ratio of purity for H_2, it means that CO and CO_2 purification system must be well-designed at high efficiency. Overall, the cost is getting more expensive, the construction is getting more complex and the size is getting bigger (EG&G Technical Services Inc., 2004).

Fundamental reactions and general fuel reaction:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \ldots \text{ Anode Reaction} \quad \textbf{(4.11)}$$

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \ldots \text{Cathode Reaction} \quad \textbf{(4.12)}$$

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O + Electrical.Energy + Heat \ldots \text{Cell Reaction} \quad \textbf{(4.13)}$$

KOH is selected for electrolyte because it is the best of alkaline hydroxides when compared by conductance.

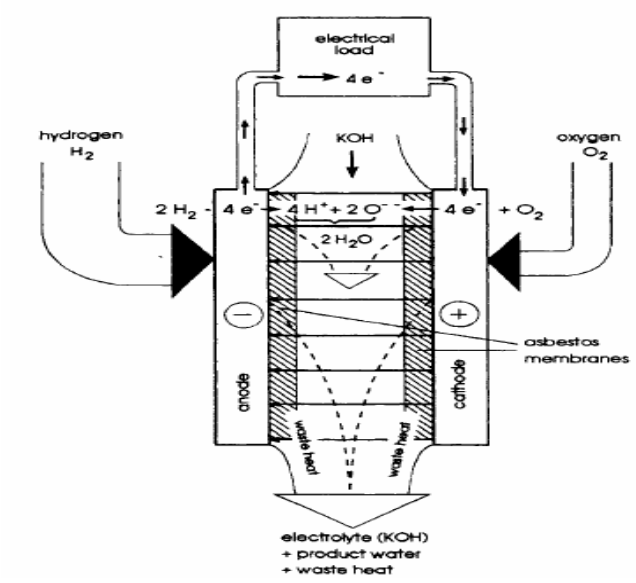


Figure 4.5 : Basic scheme of AFC

4.2.2 Phosphoric acid fuel cells (PAFC)

Typical PAFC concentration is %100 phosphoric and operation temperature is between 150 ^{o}C and 220 ^{o}C because higher temperature increases conductance and does not allow CO to harm Pt catalyst (EG&G Technical Services Inc., 2004).

When compared to general margins of acids, operating temperature of concentrated phosphoric acid is lower because of its higher relative durability as a consequence pressure of water vapor decreases and this makes water treatment simple. Silicon carbide is applied to keep acid healthy and Pt is used in anode and also cathode.

PAFCs are feasible for settled systems because they were designed and dedicated to be compatible for these systems. It is simple and possible to find advanced PAFCs in USA or Japan however recent developments on PEFC decreasing popularity of PAFCs due to better performance and better cost (Krewitt, 2005).

CO sensivity of PEFCs and AFCs are higher than PAFCs. General components are applicable for framework due to the fact that operation temperature is lower. This also simplifies design and construction of systems to export heat from Fuel Cell. Overall system efficiency is better than PEFCs on the other hand worse than SOFCs and MCFCs (EG&G Technical Services Inc., 2004).

Platinum catalyst is necessity and also reduction reactions are not as fast as AFCs. A sophisticated fuel operation system is an essential requirement by the way

performance will be upgraded. Since corrosion tendency of phosphoric acid is high, stack equipments must be complex as a result stack cost becomes higher (EG&G Technical Services Inc., 2004).

$$H_2 \rightarrow 2H^+ + 2e^- \ldots \text{ Anode Reaction} \quad \textbf{(4.14)}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \ldots \text{Cathode Reaction} \quad \textbf{(4.15)}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \ldots \text{Cell Reaction} \quad \textbf{(4.16)}$$

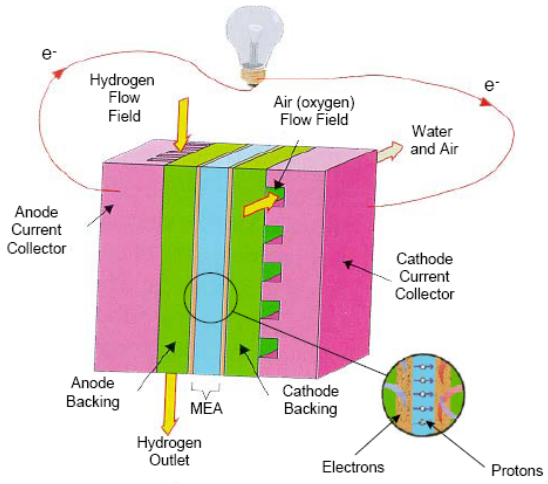


Figure 4.6 : Basic scheme of PAFC

4.2.3 Molten carbonate fuel cells (MCFC)

The nominal operating temperature is between 600 ^{o}C and 700 ^{o}C because electrolyte is consist of alkali carbonates and they build up good conductive environment by carbonate ions. High temperature also enables to use Nickel as an anode and Nickel oxide as a cathode so there is no need to noble metals to increase chemical activation (Krewitt, 2005).

Settled systems and marine industry are the main interest area of MCFCs because bigger volumes and longer start-up time could be tolerated. High cost electro-catalysts are not required due to the fact that working temperature reaches 650-700 C and also MCFC systems has ability to use CO or hydrocarbons as a fuel this raises system efficiency up to middle fifties. Besides construction will be simple since CO management is not necessary. However, high temperature must be outsourced for

automotive applications this means additional cost, weight and volume (EG&G Technical Services Inc., 2004).

Another disadvantage is electrolyte which tends to corrode other equipments as a result high-quality stainless steel must be used for cell hardware resulting high cost.

$$H_2 + CO_3^{-2} \rightarrow H_2O + CO_2 + 2e^- \ldots \text{Anode Reaction} \quad \textbf{(4.17)}$$

$$\tfrac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{-2} \ldots \text{Cathode Reaction} \quad \textbf{(4.18)}$$

$$H_2 + CO_2 + \tfrac{1}{2} O_2 \rightarrow H_2O + CO_2 \ldots \text{Cell Reaction} \quad \textbf{(4.19)}$$

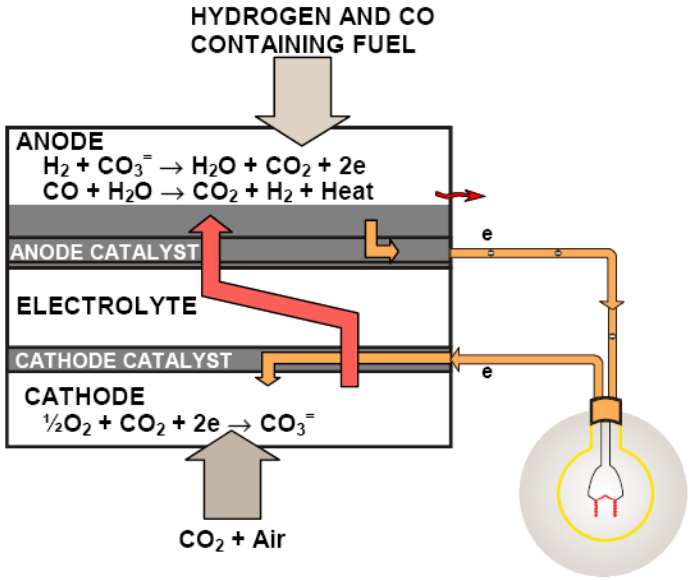


Figure 4.7 : Block scheme of MCFC

4.2.4 Solid oxide fuel cells (SOFC)

The electrolyte of SOFC is solid generally made of Y_2O_3 material. The electrolyte is not liquid it takes same advantages such as electrolyte management and limited corrosive effect. Another advantage is CO can be used as a fuel. Although the performance is good and suitable for fast working conditions, nominal operating temperature is very high about 1000 ^oC which could be solved by additional equipments as a consequence the cost increases, the volume gets bigger. If these problems are solved SOFC will be used in mobile applications however the load

applied SOFC must be a little bit steady because excessive load changes damage the unity of stack (EG&G Technical Services Inc., 2004).

4.2.5 Polymer electrolyte fuel cells (PEFC)

Short start-up and response times, lower operating temperatures and higher voltage-current capacities make PEFCs the most appropriate option for new hydrogen based energy conversion systems (Krewitt, 2005 and EG&G Technical Services Inc., 2004). A PEFC is also called Proton Exchange Membrane Fuel Cell (PEMFC) consists of four mother parts. First part is ion exchange membrane, which separates H+ and e-, is the conductive path. Second part is porous layer which works as a gas diffuser, mechanical support, pathway for electrons, channel for exhaust water from the electrodes. Thirdly, electrodes are contacts between layer and membrane.

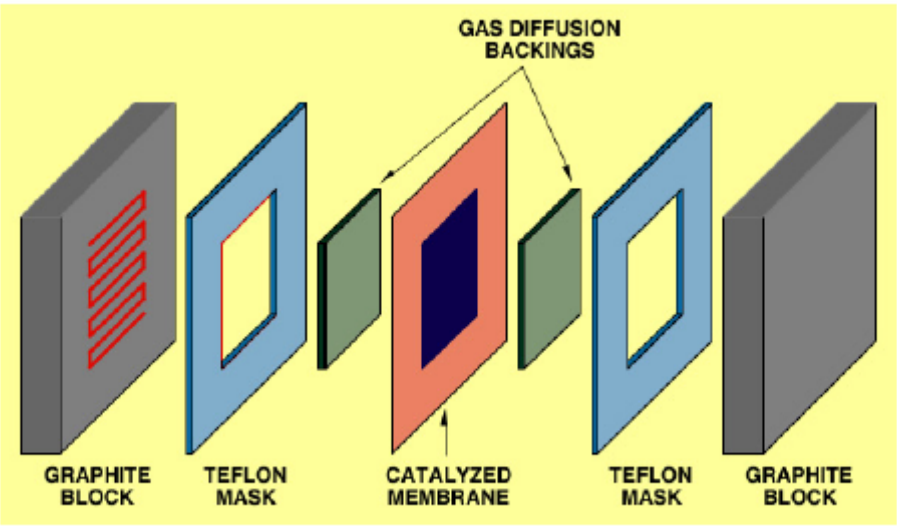


Figure 4.8 : Layers of PEFC

Hydrogen oxidized H^+ and e^- at anode. At anode side, hydrogen oxidation potential and at cathode side, oxygen reduction potential create 1V, which pulls H^+ ions from anode to cathode.

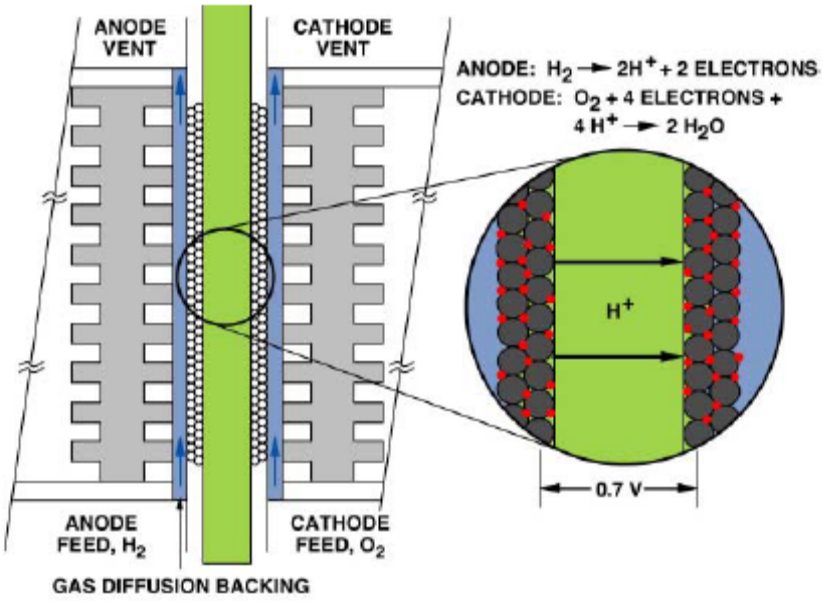


Figure 4.9 : Anode-Cathode reaction of PEFC

Theoretical operating temperature of PEMFC is between 0-90 ^oC but in practical a PEMFC works around 60-80 ^oC. PEMFCs have ability to start up fast from normal conditions because of low working temperature. However, low temperature causes CO poisoning, because CO is harmful for platinum catalyst at especially lower temperatures. Very low quantities of CO, like 2-3 ppm is allowed at 60-80 C but at high temperatures greater than 120 ^oC just adequate to stop CO poisoning. Typical membrane is made of nafion (per fluorinated sulfonic acid polymer) and it can not work properly at these temperatures since it dehydrates unless high pressure supplied (Krewitt, 2005 and Hulbert, 2009).

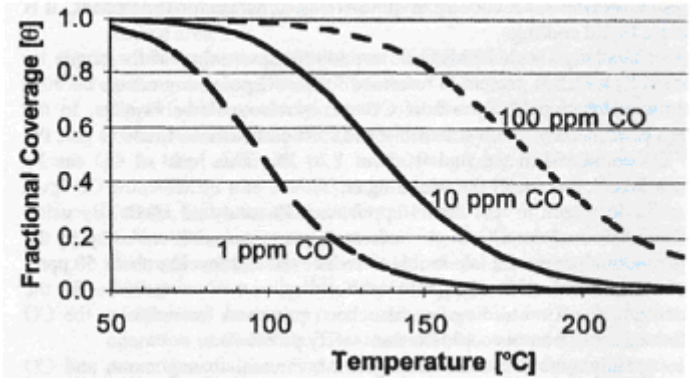


Figure 4.10 : Temperature effect on CO tolerance for PEFCs

Hence working pressure equal ambient pressure and operating temperature is below 100 C, output water is liquid. Water concentration is important for conduction ability

of electrolyte. Water treatment is a key issue for PEMFC it depends on working conditions, membrane and electrode features. Keeping working temperature stable is also a critical topic which is generally achieved by cooling water to hold temperature difference below 10 ^{o}C.

CO and S are the most effective contaminants while CO_2 and hydrocarbon fuels have relatively low effect on PEMFCs. Sulfur compounds are most damaging to the fuel cell because they adsorb onto the Pt catalyst and reduce the number of available reactivity sites for the oxygen reduction reaction. There are also some harmful chemicals for example ammonia causes membrane deterioration, alkali metals and hydrocarbons harm catalyst. They must be filtered out of the incoming air in order to prevent damage and performance loss of the fuel cell. Like the internal combustion engine, dust must be filtered out since the intake system, as well as the fuel cell, is composed of many components that are sensitive to this impurity. Aside from dust and other particulates, some harmful chemical substances must also be removed.

Table 4.1 : Effects of main toxics on different types of fuel cells

Gas	PEMFC	AFC	PAFC	MCFC	SOFC
CO	Poison	Poison	Poison	Fuel	Fuel
CH_4	Diluent	Poison	Diluent	Diluent	Fuel
CO_2 & H_2O	Diluent	Poison	Diluent	Diluent	Diluent
S (H_2S)	Diluent	Poison	Poison	Poison	Poison

Hydrogen and oxygen are two input of PEMFC. As mentioned hydrogen is supplied from hydrogen storage system but oxygen, generally is sourced from ambient atmosphere by an air intake system which is preferred to get maximum performance and efficiency from a PEMFC. The specifications of absorbed air have an emphasis on PEMFC performance such as pressure, flow-rate, humidity, temperature and purity (Hulbert, 2009).

Oxygen is one of the two inputs of fuel cell so physical condition of oxygen determines performance of the fuel cell. Likely, oxygen pressure have positive effect

on performance. For example EG&G Technical Services Inc. (2004) reported that at 93 ^{o}C, fuel cell performance increased 42 mV and 215 mA/cm^2 by changing oxygen pressure from 3 bar to 10 bar. Another example, when oxygen pressure is increased from 1 bar to 5 bar, at 50 ^{o}C, 500 mA/cm^2 and 83 mV is gained. The last example, current density of a PEMFC is increased 431 mA/cm^2 and voltage rised up 22 mV by only 1 bar changing at 80 ^{o}C. This is certain that increased oxygen pressure improves PEMFC performance but compressing of oxygen is still work and some amount of power is consumed. This means that a good optimization is needed. The additional work to compress oxygen mustn't be greater than extra work which is gained at fuel cell side. Figure 4.11 shows the effect of O_2 pressure on voltage-current characteristic of a fuel cell (EG&G Technical Services Inc., 2004).

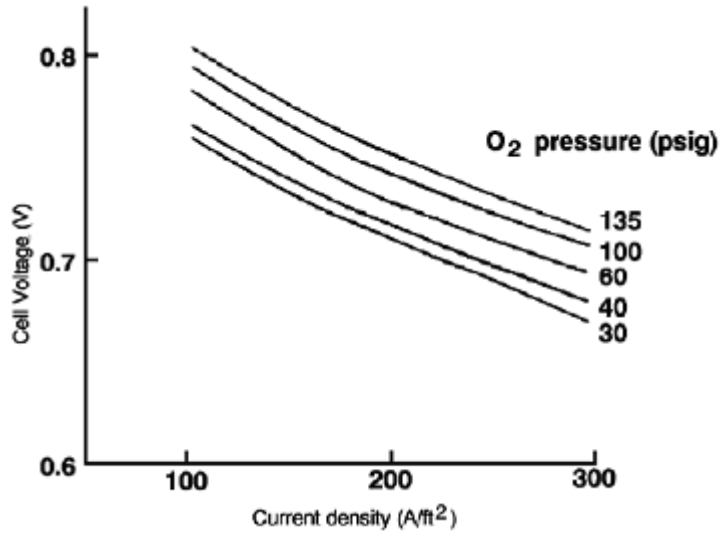


Figure 4.11 : O_2 pressure effect on PEMFC voltage-current performance

Typical PEMFC current density is 200 mA/cm^2, providing 0.78 V at 80 ^{o}C. Since mentioned above higher temperatures improve fuel cell performance for example 1,1-2,5 mV per each degree. The reason is that higher temperature decreases ohmic resistance of electrolyte and rises up reaction kinetics. Although, temperature has positive effect on fuel cell performance, too much temperature rise would cause dehydrogenation and it could decelerate ionic conductivity. So, extra heat must be removed by thermal management system for which generally air/water is preferred to keep PEMC on optimum temperature. Cooling with air or water are preferred solutions. The effect of temperature and purity is shown on below Figure. At the

same temperature pure oxygen performance is better than air and when the same air is used, higher temperature causes higher performance (Hulbert, 2009).

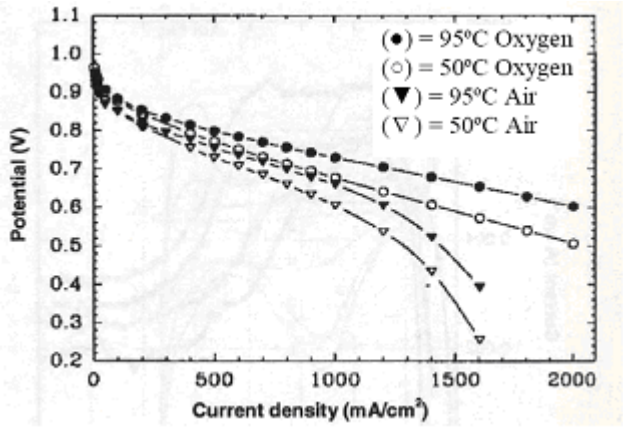
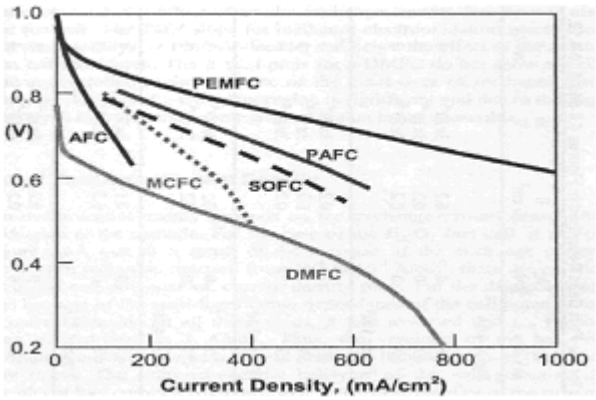


Figure 4.12 : Pure O_2 and air effect on fuel cell performance

Direct use of H_2 for PEMFC needs R&D work specifically on heat exchangers, humidifier and condenser. Existing automotive industry standards limit engine temperature at maximum 60 ^oC (EG&G Technical Services Inc., 2004). Therefore, there is a critical problem, which requires advanced water and heat treatment systems especially for very hot areas because the temperature difference will be very small.

Despite CO sensibility and thermal characteristic, PEMFCs seems as the most suitable fuel cell system for mobile applications because working temperature is low and they can easily match up with instantaneous changes in automobile applications by having quick start up/response abilities. According to Hulbert (2009) PEMFCs also have the best current/voltage capacities as shown on Figure 4.13 but there are some problems wait for to be solved. Firstly, volume and weight must be reduced. Secondly, life and reliability features must be improved. Thirdly, they must be robust to run in different working conditions. Because people travel by their own vehicles and they could move from a hot city on sea level to cold city at 1000 meters. Fourthly, cost of fuel cell and related systems must be declined to be competitive of traditional gasoline engine systems. Lastly, since their fuel is hydrogen, hydrogen related systems mainly storage systems and technical foundation must be built, standards must be published (Hulbert, 2009).



Fifure 4.13 : Typical voltage-current performance of fuel cell types

Now, only 100 hydrogen-refueling stations have been being settled in the world. Expectations say this number will increase in a short time. Still, fuel cell systems are more expensive than traditional combustion engine and cooling mechanisms also increase fuel cell stack cost but these problems are not only PEMFC's problems. These are general problems of new developed technologies.

5. HYDROGEN PRODUCTION

5.1 Water Splitting

Oceans surrounds %70 of the earth surface and water consists of hydrogen and oxygen atoms. As a result water is the first element comes in minds to generate hydrogen. Electrolysis is traditional and well-known method to split water but high temperatures and pressures are needed to get higher feasible efficiencies to generate hydrogen at industrial scale. Photo electrolysis systems are new and must be upgraded which relies on light force. Another way is photo biological hydrogen production, which is achieved by algs and bacterias. There is also another alternative way of very high temperature water splitting. When liquid water is exposed to 3000 ^{o}C, it will directly splits into molecules not boils. Details of these methods are explained below (Riis, 2005).

5.2.1 Water electrolysis

Water splits into its atoms hydrogen and oxygen by the way of electrolysis. Electrolysis is a well know process related with temperature and electrolyte. The fundamental reaction is:

$$H_2O + Electricity \rightarrow H_2 + \tfrac{1}{2} O_2 \qquad \textbf{(5.1)}$$

If operation temperature rises required total energy will increase, too. On the other hand desired electrical energy will decrease. Higher temperature will be preferred if there is another system which has ability to use exhaust heat (Riis, 2005).

KOH electrolyte is used in alkaline electrolysers which are constant systems have about 25 bar working pressure. These are general reactions of alkaline electrolysis:

$4H_2O \rightarrow 4H^+ + 4OH^-$ Electrolyte reaction **(5.2)**

$4H^+ + 4e^- \rightarrow 2H_2$ Cathode reaction **(5.3)**

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ Anode reaction **(5.4)**

$2H_2O \rightarrow 2H_2 + O_2$ Equivalent reaction **(5.5)**

Liquid electrolyte is not necessary for PEM electrolysis, which is provided by acidic polymer membrane. Since it doesn't need an electrolyte like KOH, it is safer than alkaline. Moreover, partial load ratio is bigger than alkaline. Despite having many advantages, PEM electrolysis have some problems such as short membrane life, higher cost and lower capacity.

There are also very high temperature electrolysis, like SOFC, which has nearly 1000 ^oC operating temperature. However, electrical energy requirement is lower when compared with low temperature electrolysis cells so it means general system efficiency is bigger. Higher temperature also comes with more active chemical characteristic because reactions can be reversible and high temperature enhances reactions. The problem is working ability of equipments on these higher temperatures, 900-1000 ^oC (Riis, 2005).

Production of hydrogen could be done by electrolysis of water for large amount of industrial applications. However it can be done by Hofmann voltmeter by using a few volts. For industrial applications, high-temperature and high-pressure are needed to increase efficiency of process. Typical temperature is 800 ^oC. This is very high and requires great amount of heat energy. When compared it can easily be seen that great amount of heat energy is needed to create electrical energy by hydrogen. So scientists, chemists are researching catalysts to increase reaction efficiency on lower temperatures. By the way, there will not need to get high temperatures and pressures. And also, water splits to its atoms at 2500 ^oC, it is expected that catalysts will decrease this temperature.

5.2.1 Photo electrolysis

Combinations of electrolyser and photovoltaic system can be found in today market. Product of these combinations can be electrical energy which is generated by PV system or it can be hydrogen created by electrolyser. This complex structure named photo-electrochemical cell now very popular in R&D research area. Achiveable overall system efficiency is about 16% (Riis, 2005).

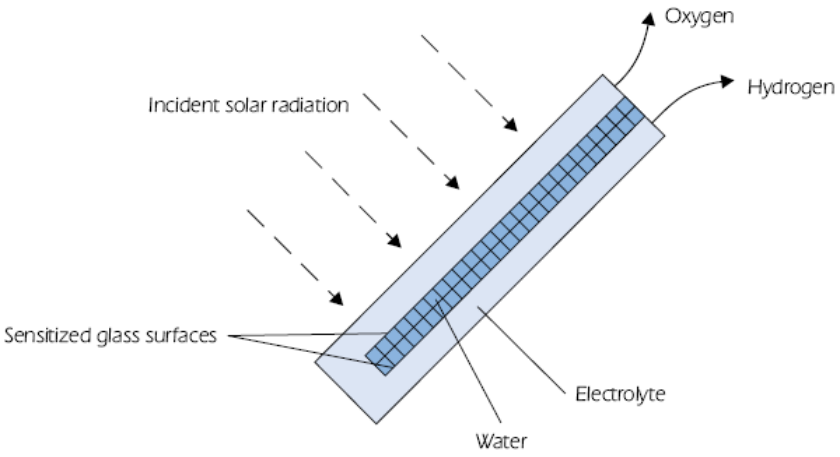


Figure 5.1 : Photo-electrolysis

5.2.2 Photo-biological hydrogen production

Photo-biological hydrogen production is made by green alg or cyanobacteria and there are two stages of it, the first step is photosynthesis and the second one is hydrogen generation. Since it is the native way of hydrogen production, being aware of nature is a significant attention for future as it would be unique solution as a result genetic engineering has focused on this way (Riis, 2005).

$2H_2O \rightarrow 4H^+ + 4e^- + O_2$ Photosynthesis **(5.6)**

$4H^+ + 4e^- \rightarrow 2H_2$ Hydrogen production **(5.7)**

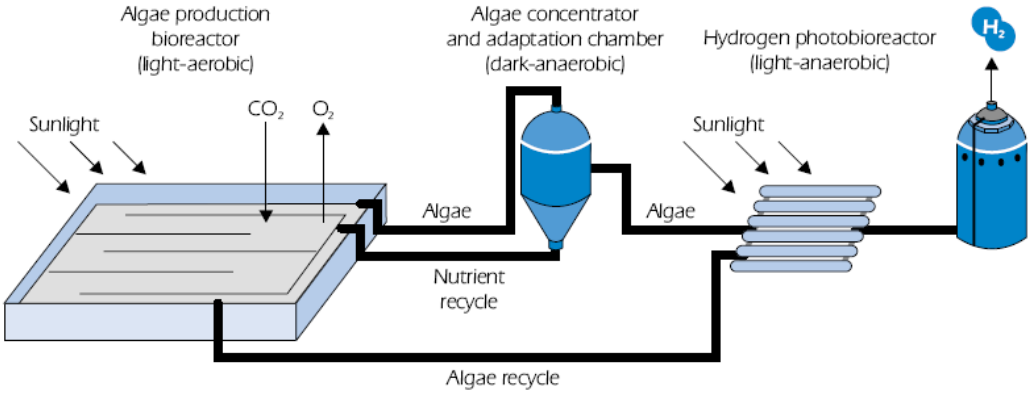


Figure 5.2 : Photo biological hydrogen production

5.2.3 High temperature water splitting

Water can be divided into hydrogen and oxygen molecules by applying very high temperatures such as 3000 ^{o}C since water jumps higher energy levels by omitting vapor state. At this temperature %10 of the water splits into hydrogen while the other %90 part recycles. High temperature can be decreased by executing other methods such as sulfur&iodine cycle. It is possible that hydrogen can be produced by thermo-chemical reaction named sulfur-iodine cycle. This method is better than splitting of water when compared according to the efficiency because recovery and reuse of the sulfur and iodine is possible (Riis, 2005).

Steps of sulfur-iodine cycle are listed below.

$$2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI \ldots @120^oC \quad \textbf{(5.8)}$$

$$2HI \rightarrow H_2 + I_2 \ldots @450^oC \quad \textbf{(5.9)}$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + \tfrac{1}{2}O_2 \ldots @850^oC \quad \textbf{(5.10)}$$

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad \textbf{(5.11)}$$

Despite being well-known and conventional, this method has challenges like high temperature non-corrosive materials and keeping conditions of high temperature hydrogen.

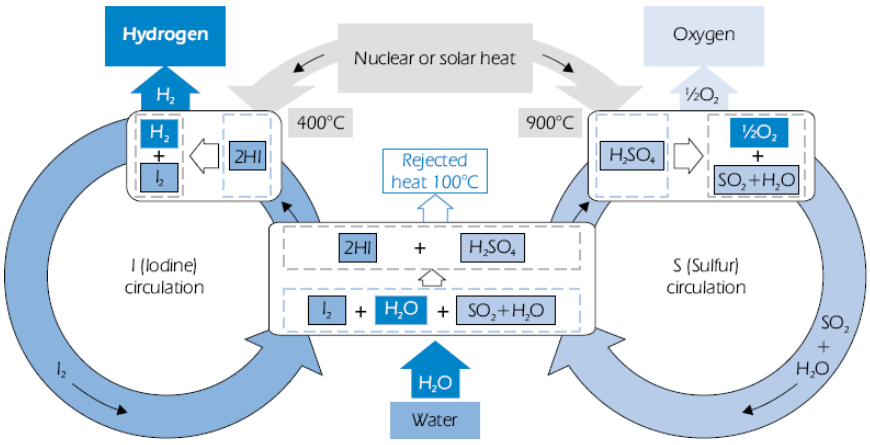


Figure 5.3 : Sulfur-iodine cycle

5.3. Hydrogen Production From Fossil Fuels

Hydrogen production from fossil fuels is divided in two types according to the fossil fuel, natural gas and coal. Steam reforming is one of the hydrogen production ways from natural gas, which typically occurs at 700-850 ^{o}C and 3-25 bar. Generally, in industry methane reformer is used to make hydrogen. The process consist of two steps; Endothermic reaction and water-gas shift reaction is given below (Krewitt, 2005).

$$CH_4 + H_2O + Heat \rightarrow CO + 3H_2 \quad \textbf{(5.12)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Heat \quad \textbf{(5.13)}$$

The other way is Partial Oxidation by means of an endothermic oxidizing reaction of fossil fuel. The main endothermic reactions of process are listed below.

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO + 2H_2 + Heat \quad \textbf{(5.14)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Heat \quad \textbf{(5.15)}$$

Since there is no need to heat to activate the reactor, so there will not be an additional heating system. And the last way is auto-thermal reforming which is the combination of steam reforming and partial oxidation. Steam reforming is endothermic and partial oxidation is exothermic but auto-thermal reforming is exothermic reaction. Typical operation temperature is 950-1100 ^{o}C and pressure is 100 bar (Riis, 205).

The coal can be used to produce hydrogen but it requires various gasification steps such as fixed bed, fluidized bed and entrained flow. Solid carbon is transformed to carbon monoxide and hydrogen according to the given endothermic reaction. CO is converted to the CO_2 again water-gas shift reaction.

$$C_{(Solid)} + H_2O + Heat \rightarrow CO + H_2 \quad \textbf{(5.16)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 + Heat \quad \textbf{(5.17)}$$

Recent surveys are going to research methanol or natural gas based small units to feed fuel cells. Not only methanol and natural gas are tried but also other fossil fuels such as propane, gasoline, diesel fuel etc. are tried to find best alternative.

In reforming processes and coal based hydrogen production as fossil fuels include Carbon, C atoms pass through to the atmosphere in CO_2 form. As a result, even though using hydrogen energy is an eco-friendly way, producing hydrogen will not decrease CO_2 emission on the contrary it may increase CO_2 ratio of atmosphere. A typical refinery emits about ten thousand tons of CO_2 which can be divided into two parts; great amount of CO_2 causes from process and while the rest causes from burning fossil fuels to heat up reactors.

Although, some investors claim reforming would solve the problem of transportation of hydrogen source and steam reformer with methanol tank could be used instead of massive hydrogen tank, market leaders do not seemed to change their ways, because they believe this application is not possible.

Unit price related with the capacity of production. While the cost of hydrogen reaches maximum a few $ per kg small scale hydrogen production is more expensive than others

However, there are several challenges associated with this technology:

- High temperature is needed to achieve reforming as a consequence start up will slow and expensive materials, which have ability to work under high temperature are required.
- Low temperature PEMFC needs serious CO-elimination systems because they harm PEMFC. SOFC and MCFC are not affected but operation at higher temperatures slows up start up and needs huge insulations and expensive materials.
- The thermodynamic efficiency of the reaction is between 70% and 85% and purity of hydrogen determines this efficiency.
- Platinum is the fundamental element of low temperature fuel cells and platinum is a very expensive material to use. A sample fuel cell includes 20-30g of platinum.

5.4. Hydrogen Production From Biomass

Steps of production processes of hydrogen from biomass:

- Thermo-chemical gasification coupled with water gas shift.

- Fast pyrolysis followed by reforming of carbohydrate fractions of bio-oil.
- Direct solar gasification.
- Miscellaneous novel gasification process.
- Biomass-derived syn-gas conversion.
- Supercritical conversion of biomass.
- Microbial conversion of biomass.

$$Biomass + O_2 \rightarrow CO + H_2 + CO_2 + Energy \quad \textbf{(5.18)}$$

There are three methods to generate hydrogen from biomass or waste streams: biomass gasification, steam reforming and biological transformation. Biological transformation can be made by two ways. Firstly, fermentative hydrogen generation, which requires a type of bacteria, has ability to converse organic substance to hydrogen by its enzyme system. Light is not necessary for dark fermentation on the other hand photo fermentation needs light. Organic substance source is generally waste streams. A type of bacteria decomposes hydrocarbons and hydrogen. They generate CO_2 as a result of chemical reaction. This new method has been being tested in North East, Pennsylvania. The second one is biocatalysed electrolysis. Wastewater or plants could generate hydrogen by using microbial fuel cells (Riis, 2005).

6. HYDROGEN STORAGE SYSTEMS

Hence, it enables to improve energy efficiency and decreases harmful gases emission, fuel cell electrical vehicles are very important for earth future. At that point, hydrogen storage is one of the main issues for FCEVs development. Because hydrogen can be filled into vehicle's fuel tanks and it can be consumed easily, like existing petroleum technology. Many researches have been made and different solutions have been found to solve this serious technical difficulty. There are some new solutions except classical compression or liquefaction. For example, chemical alternatives such as metal hydrides, ammonia and physical adsorption solutions like carbon nanotubes. Scientists have been searching the best storage system according to critical features; safety, efficiency, reversibility, harmful emission and cost.

There are many aspects of the best hydrogen storage system. One of the most important features, which have to be satisfied by the best option is safety, because hydrogen is a flammable and explosive chemical. Transportation of hydrogen from central plants to distribution stations, keeping in station, transferring from station to vehicle and storing in vehicle truck are important processes related with hydrogen storage. These processes are very critical issues because of safety, efficiency and greenhouse gas emission. Firstly, the hydrogen storage system of a vehicle must be safer, because human health is the most important thing. Everyday, many accidents, generally caused by people fault, happen. Manufacturers compete with each other to make the safest car, governments force people to obey traffic rules and have strict punishments. There are many educations, brochures, TV films to take care of people interest.

Secondly, efficiency is the other important parameter, since it is not possible to use all energy, which was stored before, without any losses. Hydrogen is a special energy source, which is produced not mined so wasting hydrogen means wasting energy directly. Today, hydrogen is produced commonly from fossil fuels at lower efficiency ratios, around 40-60%. The best system should have maximum hydrogen capacity at minimum weight&volume. The dissociation temperature should be low

and average pressure is acceptable. Released and emitted heat should be low since lower energy losses aimed.

Reversibility is another important requirement, because for on board usage, hydrogen will be discharged on vehicle and it could be charged on distributed stations like traditional oil-gas stations. Today, at conventional stations oil tank of a car can be fully filled maximum in 5 minutes so charging kinetics must be as fast as existing oil systems. Ideal hydrogen storage systems must be durable against moisture and oxygen because corrosive effect harms storage systems, decreases system efficiency and life. Next sections are going to define and compare theses technologies and find best available technology according to their features (Sakintuna, 2006).

Thirdly the best option should decrease Greenhouse Gas Emission. Carbon dioxide is the worst end-product which harms earth and nature so the best option must decrease greenhouse gas emissions.

The last and may be the most important point is the cost. FCEVs will only be preferred if their life cycle cost is better than traditional ICVs. For example, today, diesel engine vehicles consume less volume per kilometer than gasoline vehicles. And the diesel oil cost is lower than gasoline. On the other hand, purchasing cost of a diesel vehicle is generally higher than a gasoline vehicle, so this means there is a trade-off. People, generally merchants, who travels very much, prefers diesel or people, who wants to get more performance and does not care money, prefers gasoline vehicle. In conclusion, the best storage option must be cost-effective to be feasible.

Density of hydrogen is very low, 0.089 kg/m^3 , so a large volume of gas includes very little amount of mass. Nevertheless hydrogen's energy per mass ratio is very high since scientists are very interested in hydrogen. There are three main storage methods; compressed, liquefied and solid. Since hydrogen is in gas form at ambient temperature, it can be pressurized in tanks which needs compression energy. Secondly, hydrogen can be liquefied at very low temperatures and can be stored into well-insulated tanks. This process also requires compression and cooling energy. Thirdly, hydrogen can make strong or weak interactions (Covalent bonds and Van Der Waal interactions) with other chemicals and stored into solid form. It is also a difficult manner to store hydrogen into a solid chemical. Because interaction should be easily breakable, otherwise there will be much more energy needed to release

hydrogen than storing. Average value for interaction is 20 kcal/mol which can be accepted as a moderate energy, less than covalent bond and more than weak bond (Di Profio, 2009). At this chapter, common hydrogen storage methods will be investigated according to their possible use in electrical vehicles.

6.1 Gas

Storing hydrogen in gas form is the most common way, which could be done by composite tanks or glass microspheres. Despite having a large industrial scale, composite tanks have question marks for automobile applications such as safety. Although glass micro spheres offer high gravimetric density, high temperature requirement makes it non-useful for car industry (Riis, 2005).

Hydrogen can be stored in fiber composite tanks, which have common usage in industry since the technology is advanced and old. Typical compression pressure is about 350-700 bar. Gardener (2009) described general required energy to pressurize from 20 bar to 350 bar is 1.05kWh/kg H_2 and 1.36 kWh/kg for 700 bar when compressed in central process. When calculated for on-board compression these values increase to 1,7 and 6,4 kWh/kg H_2 because of lower compressor and system efficiency in lower capacities. Lower Heating Value (LHV) for hydrogen is accapted 33,3 kWh/kg so compression energy equals 5-20 % of LHV. Figure 1 shows the relation between pressure, temperature and stored hydrogen capacity. High pressure is safer for steady applications on the other hand it has serious safety problems for automobile industry in case of any accident. (Astbury, 2008) Volume and shape of tanks is also another disadvantage of mobile applications. They have large volume and weight so it is hard to insert a large and cylindrical tank in to a car. (Jain, 2009)

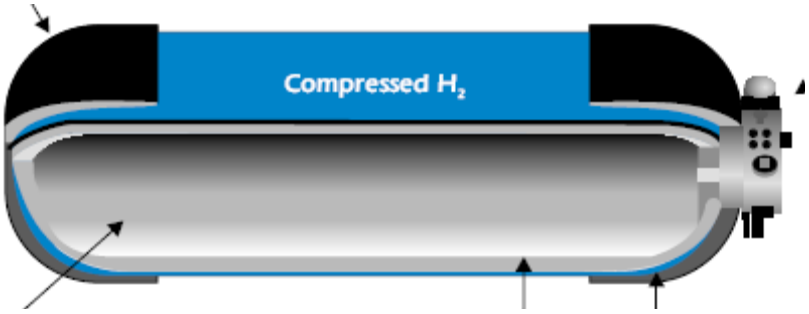


Figure 6.1 : Compressed hydrogen tank

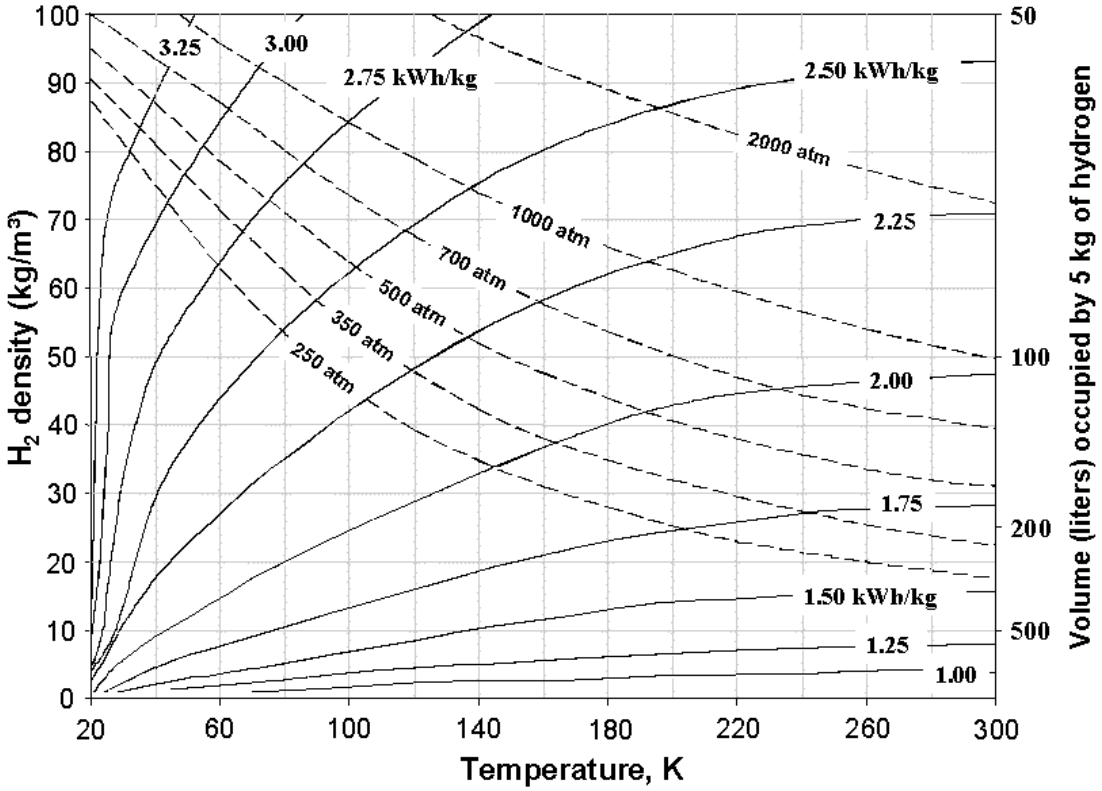


Figure 6.2 : Pressure effect on compressed hydrogen storage

Secondly, glass micro spheres with high gravimetric density are new type of hydrogen storage systems. Storing consists of three steps. Firstly, hydrogen is filled at 350-700 bars into spheres at about 300 C. After that, micro spheres are cooled until room temperature and they are inserted low pressure tank. Finally, on car the low pressure tank is heated to manage hydrogen flow at 300C because hydrogen discharging rate is low and irregular at room temperature so additional heat must be given to tank. Another disadvantage is that despite having high gravimetric density volumetric density of glass micro spheres is still low. (Riis, 2005)

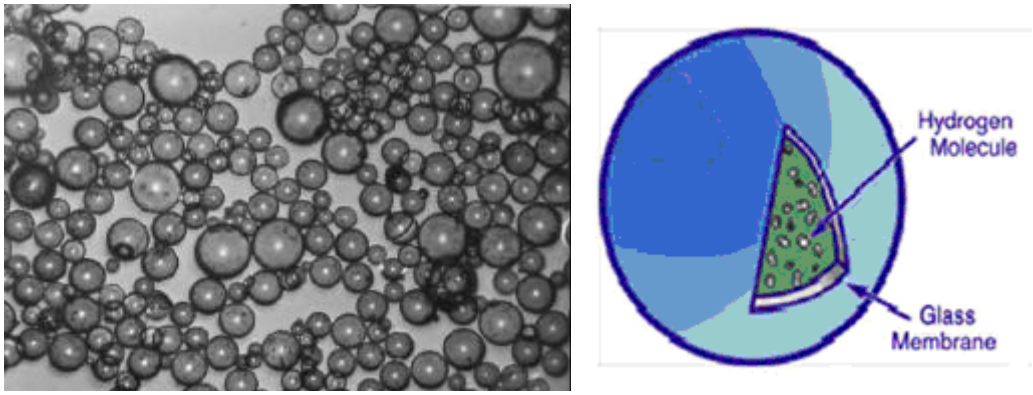


Figure 6.3 : Glass microspheres

Energy consumption for compression and efficiency of the system are other disadvantages of gas hydrogen storages systems. Generally, 1.15 kWh/kg is needed to fill 350 bar tank at 440 bar and 1.47 kWh/kg is needed to fill 700 bar tank at 880 bar charging pressure. Compressors are used to pressurize hydrogen into gas form. The reciprocating compressors are the most popular ones. The compressor consists of two main sides one them is electrical motor, which has %92 efficiency while the other one is mechanical compressor while its efficiency is less than %55. A a consequence, overall system efficiency drops %52 for 440 bar, %49 for 880 bar.

6.2 Liquid

Hydrogen storage in liquid form differs in four main types. One of them is liquid condition of pure hydrogen while the other types consist of combinations of chemical materials such as $NaBH_4$ solutions, rechargeable organic liquids and liquid anhydrous ammonia. In this part $NaBH_4$ solutions will not be explained, they will be introduced at borohydrides section.

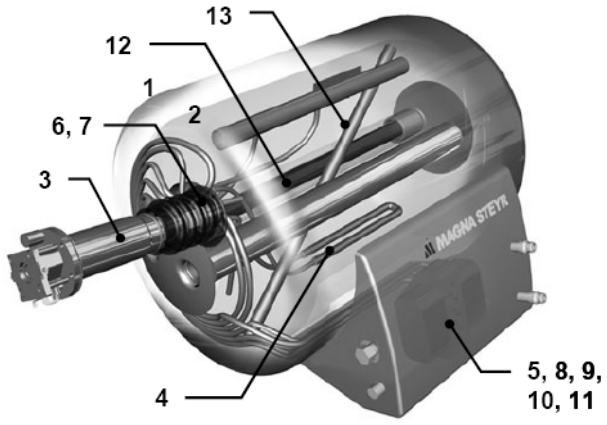
Liquid hydrogen (LH_2) is used as a rocket fuel since the density of boiling point is very low and specific thrust is very high. These are main reasons for being rocket fuel but also heating energy per mass ratio and specific heat constant are very high. Despite having the highest energy per volume ratio, a great amount of energy which equals 40% of its combustion energy (Lower Heating Value is accapted 33.3 kWh/kg), is needed to liquefy and keep it in liquid form. (Sherif, 1997)

Liquid hydrogen storage has extra producing requirements consequently more power is needed when compared with pressurize. Average energy need to liquefy hydrogen at 300 K, 1 bar is about 10-13 kWh/kg. Recent developments reveal that 7 kWh/kg is achievable by magnetic active regenerative liquefiers. When compared with other technologies even if it reaches 7 kWh/kg this will be still high. (Gardiner, 2009)

Super-insulated cryogenic tanks are used to keep liquid hydrogen for mobile applications. Since hydrogen boil-off losses become a concern, cryogenic tanks are required to minimize these losses. A typical shape of cryogenic liquid hydrogen tank is given below. (Krainz, 2003) The tank is generally made by stainless steel or aluminum alloy as they are compatible with hydrogen. There are two layers of the tank and there is a gap between for heat insulation. Typical pressure is 2-4 bar.

Typical boiling temperature is nearly -253 ^{o}C. In spite of theoretically gravimetric density is %100, achievable value is about %20 wt. (Riis, 2005)

Liquefied hydrogen storage system is risky for mobile applications because there is a big difference between hydrogen storage tank and ambient temperature. If an accident happens and tank is damaged, there will be sudden changes, which causes explosion of hydrogen. (Astbury, 2008)



1 Outer tank
2 Inner tank
3 Coupling (Johnston-Cox)
4 Heater
5 Heat exchanger
6 Cryogenic filling valve
7 Cryogenic return valve
8 Pressure regulation valve
9 Shut-off valve
10 Boil-off valve
11 Safety relieve valve
12 Support post
13 Liquid level sensor

Figure 6.4 : Liquid hydrogen tank

Alternatively, organic liquids could be used to generate hydrogen by a catalytic process called dehydrogenation. Examples are given below.

$$C_7H_{14}(l) \Rightarrow C_7H_8(l) + 3H_2(g) \qquad @\ 300\text{-}400\ ^{o}\text{C} \qquad \textbf{(6.1)}$$

$$C_{10}H_{18}(l) \Rightarrow C_{10}H_8(l) + 5H_2(g) \qquad @\ 200\ ^{o}\text{C} \qquad \textbf{(6.2)}$$

Although, operating pressure is low and density is quite good (%6 wt), the temperature is high and product of reaction is easily flammable and explosive. This means there is a real safety problem. On the other hand, explosive product organic liquid must be removed to regeneration process. (Riis, 2006)

The last type of liquefied hydrogen solution is liquid ammonia. The ammonia is one of the common chemicals in the world which has well-industrialized generation and well-organized distribution network. It could be separated into nitrogen and hydrogen molecules by nickel catalyst. Theoretical achievable density is 17% wt. Like organic liquids, reaction output nitrogen is toxicity and creates security

problems. Moreover, fuel cell must be prevented from NH_3 since it harms fuel cell. (Di Profio, 2009)

$$2NH_3 \rightarrow N_2 + 3H_2 \quad \textbf{(6.3)}$$

In conclusion, despite being able to get higher densities by storing hydrogen in a liquid state with different strategies, there are critical problems wait stable solutions. The amount of energy required to produce, cool and liquefy hydrogen gas must be reduced. Advanced safety systems must be developed and adapted into on-board distributed usage as cheap as possible since organic liquids and liquid ammonia have explosive and harmful outputs.

6.3 Solid Hydrogen

Hydrogen could be adsorbed by carbon materials or other high surface area materials and it could be absorbed by metal hydrides in solid space. Since gas form of hydrogen require high pressures and liquid storage needs cryogenic temperatures, solid hydrogen systems, especially metal hydrides, keeps its critical position in researchers mind. Storage of hydrogen by carbon materials and other high surface area materials are occurred in physisorption, which means that hydrogen interconnects with these materials by creating new weak bonds. This is a well-know method, on the other hand, hydrogen absorption and desorption by metal hydrides is a novel technology.

Hydrides are new chemical systems on which hydrogen changes its bond and makes another bond with other chemical elements. For example, hydrogen makes new bonds with Mg^{+2} and this reaction produces MgH_2 an example of High Temp Hydrides or reaction with H^+ and $LaNi_{5\text{-}6}$ and Low Temp Hydride is produced $LaNi_5H_6$. Operation temperatures and pressures of metal hydrides are quite low, moreover, some of them may work at ambient temperature and pressure.

6.3.1. Carbon and high surface area materials

The opportunity of hydrogen storage on carbon materials, which is an old and known method, has invented in 1985. There are four main types of carbon materials: Activated carbon, Graphite, Graphene and Carbon nanostructures. Hydrogen makes weak bonds at the molecular level with other chemicals in Single Walled Carbon

Nanotubes (SWNTs)., these connections also named “physisorption”. Zeolites, metal oxide framworks and clathrate hydrates are three popular types of high surface area equipments. (Ströbel, 2006)

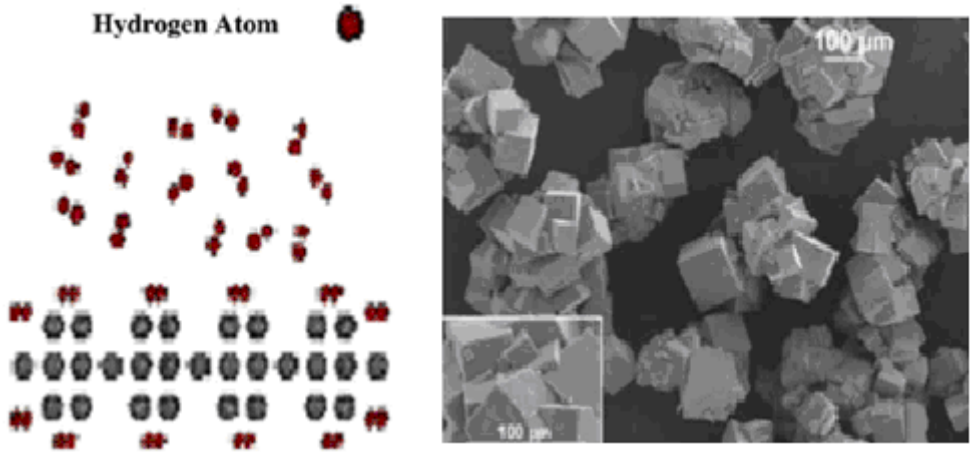


Figure 6.5 : Physisorption and shape of carbon materials

Although pressurized and liquid hydrogen storage systems are used automobile industry, security and hydrogen supply still problems, which must be solved. Solid hydrogen storage systems have advantage since they do not include pure hydrogen.

Storing hydrogen in different types of carbon materials is old and well-known technology. There are many types of carbon materials such as Activated carbon, graphite, graphene and carbon nanostructures. Activated carbon is made of small graphite crystal and amorphous carbon at higher temperatures. It is cost-effective and industrial; hydrogen storage capacity depends on microstructures. Graphite is another type of carbon material which looks like sheet, bonded via Van Der Waals interconnection. Despite being cheap and having high alfa, graphite has lower area so storage capacity is low. Thirdly, graphene, which consists of carbon hexagonal cells, doesn’t have ability to store hydrogen. There are two kinds of carbon nanostructures, fullerene and carbon nanofibers. Carbon nanotubes, which seems rolled single level of graphen, is a type of fullerene which has good hydrogen capacity like %4 at 100bar. There are many factors which affect hydrogen capacity of carbon nanotubes such as pretreatment, geometry, structure, purification, pressure and temperature. (Ströbel, 2006)

Hydrogen storage on carbon materials is physisorption called new Van Der Waals interconnection between gas and solid. The more surface means the more adsorption. The aim on physisorption is sturdy adsorption at the same time easy desorption.

Another way of storage is chemisorption which occurs on π bonds, needs very high pressures range from 500 bar to 30000 bar and higher temperatures (300-400 ^{o}C) As a result chemisorption is not a useful way to store hydrogen. (Ströbel, 2006)

Metal oxide frame works which consists of ZnO, clathrate hydrates and zeolites are the other types of high surface materials. Especially, some modification could be made on relatively high surface area of metal oxide frame works. Zeolites are also famous with non-H_2 keep feature consist of aluminosilicats. (Riis, 2005)

Clathrates, which may have CH_4 or CO_2, consist of H_20 configuration. Hydrates could be used to store hydrogen, the ratio is low like 4% but also the reaction time is too long sometimes it takes several weeks. Published researches about hydrogen storage capacity of clathrates are made in 2002. Recent surveys have tried to decrease time from days to minutes. Researchers use a new method which consists of nanotechnology and chemical catalyst and does not include surface active addictives which rise system weight. (Sandrock, 2008)

60-120 bar pressure is enough to compress hydrogen in hydrate form and also -8/-9 ^{o}C temperature level is also adequate to keep hydrate form. The fundamental component is water consequently there is a cost advantage. The main problem is reaction is very complex and the required time is too much. (Di Profio, 2009)

6.3.2. Metal hydrides

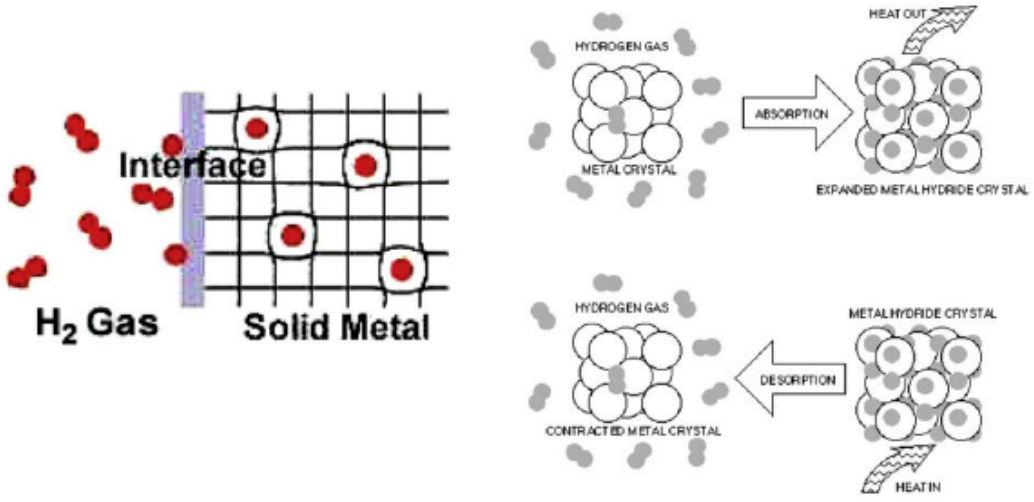


Figure 6.6 : Hydrogen absorption and desorption by metal hydrides

Metal hydrides are novel, hydrogen storage systems with different volumetric and gravimetric densities. Their storing and releasing fundamentals are absorption and desorption. (Figure 6.6) While some types of them have reversible characteristics, some types need central refueling stations. When compared with other hydrogen storage methods, they have the highest energy density per volume ratio. (Di Profio, 2009)

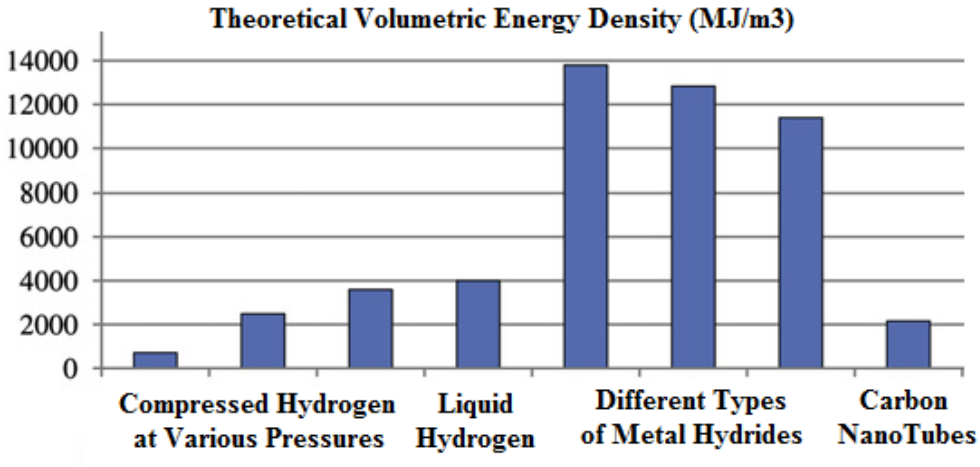


Figure 6.7 : Volumetric energy density of different types of storage systems

There are three main types of metal hydrides. One of them is water (H_2O) reactive chemical hydrides, which are activated with water, then they also called slurries. Another type is thermal reactive chemical hydrides such as NH_4BH_4, which is divided into H_2 molecules by applying high temperatures. The last type is rechargeable metal hydrides on which scientists have focused on, has a wide range family tree.

Water (H_2O) reactive chemical hydrides also called slurries which means when a solid and a liquid are mixed to produce liquid blend. Since their form is semi-liquid they can be pumped which is a critical advantage, because it makes possible to use existing fuel distribution and transportation system by making a few modifications. The problem is, not being easly controllable of water-hydride reaction. As seen in reactions given below, chemical hydride interacts with water consequently; hydrogen, base and heat are generated. Typical pressure is nearly 7 bar and typical temperature is about 300 ^oC so these slurries also called high temperature hydrides. Hydrogen storage differs from 5.2%wt to 7.8 %. (Riis, 2005) In spite of high desorption temperature, like 300 ^oC at atmospheric pressure, MgH_2 is the best

performer in slurries because of its advantages such as, good reversibility, low-cost, being high-resistive to heat and ability to absorb vibration. Na, Li and Be are lighter than Mg but their reaction kinetics and thermodynamic characteristics worse than Mg.

Table 6.1 : Reaction of basic slurries and their storage density

Reaction	Storage Density, wt % H_2
$LiH + H_2O \Rightarrow H_2 + LiOH$	7,8
$NaH + H_2O \Rightarrow H_2 + NaOH$	4,8
$MgH_2 + 2H_2O \Rightarrow H_2 + Mg(OH)_2$	6,5
$CaH_2 + 2H_2O \Rightarrow H_2 + Ca(OH)_2$	5,2

To decrease high desorption temperature of MgH_2 (Figure 6.8), magnesium can be used with transition elements (Ni, Cu, Sc, Y, Fe, Mn, Co, Ag), non-transition elements (Li, Al, AI, Ga, In) and rare-earth elements(La, Ce, Mm). Sakintuna (2006) reported the effect of alloying on MgH_2. Hollow lines refer to alloyed MgH_2 and the bold lines refer to alone MgH_2.

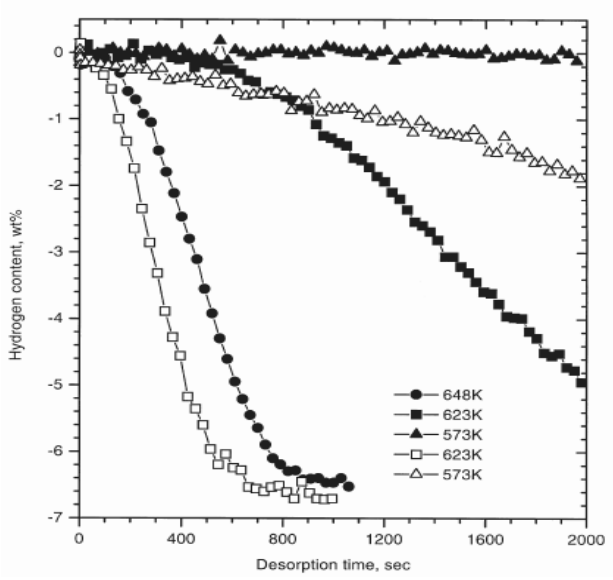


Figure 6.8 : Effect of catalyst on magnesium desorption temperature

Thermally active chemical hydrides are the second type of chemical hydrides. For example, ammonia borane is a type of metal hydride, which splits up into new chemical construction at four steps by exposed to high temperatures. As seen on table storage density ratios are quite good but reactions are not reversible and heat

level increases at every steps. Moreover, borane is a poison and it may be harmful for fuel cell and must be carefully removed or recycled.

Table 6.2 : Decomposition steps of ammonia borane

Desorption Reaction	**Storage Density, wt % H_2**	**Temperature, ^oC**
$NH_4BH_4 \Rightarrow NH_3BH_3 + H_2$	6,1	$^oT < 25$
$NH_3BH_3 \Rightarrow NH_2BH_2 + H_2$	6,5	$^oT < 120$
$NH_2BH_2 \Rightarrow NHBH + H_2$	6,9	$^oT > 120$
$NHBH \Rightarrow BN + H_2$	7,3	$^oT > 500$

The last type is rechargeable hydrides on which researchers have focused. Because their reactions are reversible and hydrogen storage capacity is moderate. Moreover, they are safer systems since operation pressure and temperature are low. Reversible hydride reaction is given Eq. 6.4.

$$M + xH_2 \Leftrightarrow MH_x + Heat \qquad \textbf{(6.4)}$$

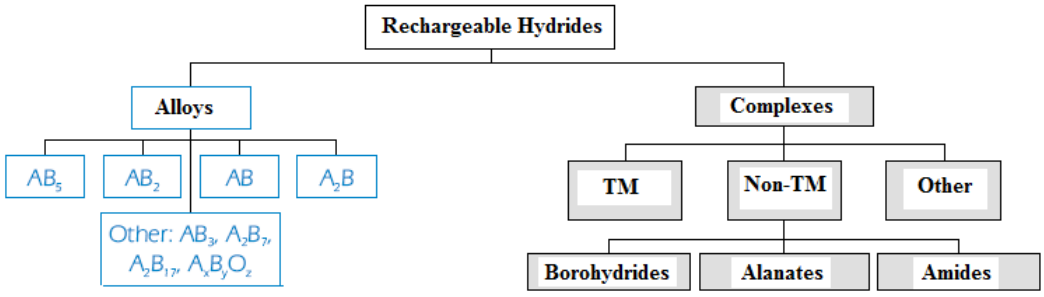


Figure 6.9 : Common types of rechargeable hydrides

Rechargeable hydride family tree is seen on Figure. Alloys such as lanthanum nickel ($LaNi_5$), mischmetal nickel ($PrNi_5$), FeTi, are called low temperature hydrides (about 20 bar, 20 ^oC). Their gravimetric capacity is also low, like 1.5% wt. They have different characteristics, for example, AB_2 type (A: Ti, Zr and B:V, Cr, Mn and Fe) has higher storage capacity, lower cost and longer life. On the other hand, AB_5 type is more durable and its reaction kinetic is better than AB_2. For instance, very little

oxygen concentration may harm AB_2 type, but it only decreases hydrogen storage capacity of AB_5 type. Repeatability is a problem for alloys, because after a few cycle their storage capacity starts to decrease. To improve the performance of alloys, many techniques, for example ball milling, alloying, catalysts etc. are applied.

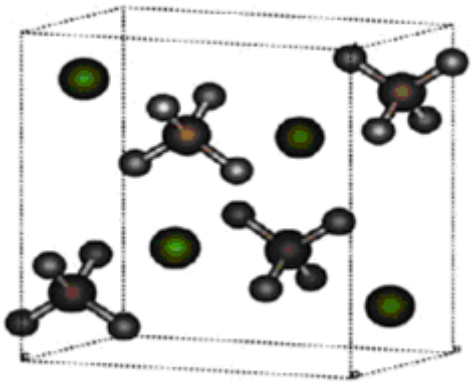


Figure 6.10 : Structure of complex hydrides

Complex hydrides have great importance since they assumed the best choice of storage in both mobile and stationary hydrogen systems. (Riis, 2005) Despite $LiAlH_4$ has the best storage capacity, especially $NaAlH_4$ activated by Ti catalyst, stands on the top of the candidate list. Because desorption temperature of $NaAlH_4$ is low, reversibility is better and it is commonly industrial. Sakintuna (2006), reported that Ti accelerates $NaAlH_4$ reaction kinetics five times shorter. Similarly, Riis (2005) and Sakintuna (2006) claimed that storage density and reaction kinetic must be increased by different types of catalysts and the cost of $NaAlH_4$ must be reduced. Basic structure of $NaAlH_4$ is given in Figure. (Jain, 2010)

Table 6.3 : Storage density (wt%) and decomposition temperature of basic alanates

Alanate Type	**Storage Density, wt % H_2**	**Temperature, ^oC**
$LiAlH_4$	10,6	190
$NaAlH_4$	7,5	100
$Mg(AlH_4)$	9,3	140
$Ca(AlH_4)$	7,8	>230

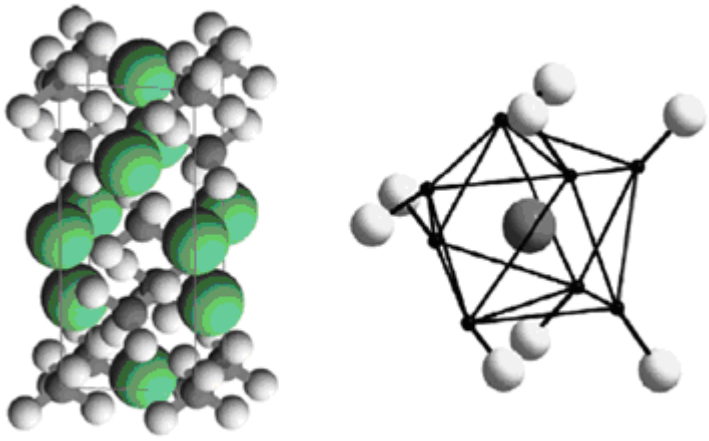


Figure 6.11 : Basic structure of sodium-alanates ($NaAlH_4$)

Borohydrides are another type of Non-TM complex hydrides. $LiBH_4$ and $NaBH_4$ are the first borohydrides, which were discovered at 60s. $NaBH_4$, which is also mentioned in liquid hydrogen storage section, has common usage areas such as textile and paper manufacturing and also it is used as a disinfectant in organic synthesis. (Material Matters, 2007). Basic structure of lithium borohydride and sodium borohydride are given in Figure.

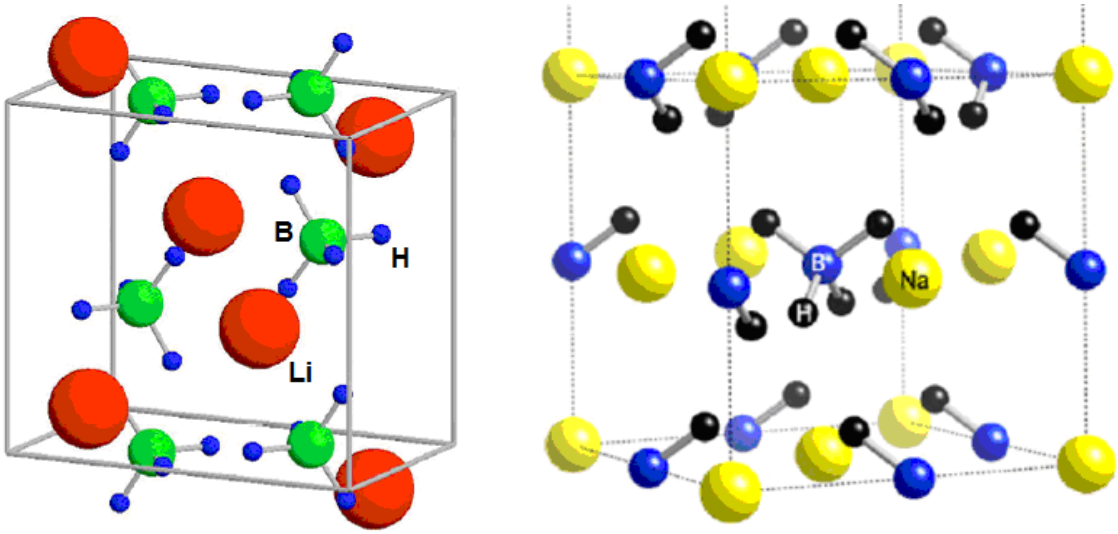


Figure 6.12 : Basic structure of $LiBH_4$ and $NaBH_4$

As seen on table borohydrides have better performance on storage than alanates.(Riis, 2005) Because of lower working temperature and pressure, they are safer than alanates. However, they have some critical disadvantages also.

Borohydrides don't as reversible as alanates because they are more stable and dehydrogenation temperatures are very high. For example $LiBH_4$ could reach 18%wt ratios but necessary pressure and temperature is very high. (300-600 ^oC). They are also very expensive materials. Jain (2010) reported that typical $NaBH_4$ storage density is %11 wt. Hydrogen desorption performance can be upgraded by catalyst. Park (2007) proved the effect of four different catalyst ("a" to "d" refers to various catalysts) which is shown on Figure. As it can be concluded from graphic released hydrogen increases from "a" to "d".

$$NaBH_4(l) + 2H_2O(l) \rightarrow 4H_2(g) + NaBO_2(s) \quad \textbf{(6.4)}$$

Table 6.4 : Storage density (wt%) and decomposition temperature of basic borohydrides

BoroHydrides	**Storage Density wt.%H_2**	**Temperature, ^oC**
$LiBH_4$	19	300
$NaBH_4$	11	350
KBH_4	7	125
$Be(BH_4)_2$	21	125
$Mg(BH_4)_2$	15	320
$Ca(BH_4)_2$	12	260

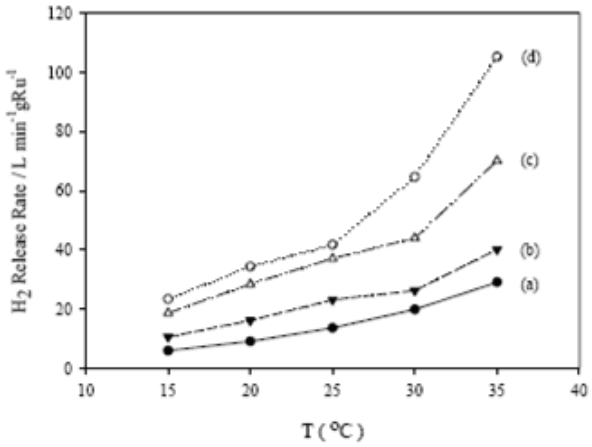


Figure 6.13 : Catalyst effect on $NaBH_4$ desorption

The essential problem of sodium borohydride is $NaBO_2$ management. $NaBH_4$ solution could be consumed on vehicle but output of chemical reaction, $NaBO_2$ must

be removed and re-cycled as a result additional systems are needed which increase volume, mass and cost.

Amides have higher hydrogen capacity (8%wt) but operating temperatures are medium or high and their reaction kinetic is low unless used with catalyst. (Jain, 2010) The most popular amides are lithium, magnesium, calcium and sodium amides and also Li-Mg-N-H, Li-Ca-N-H and Li-Al-N-H are the other types of amides. According to Material Matters (2007) hydrogen storage capacities and desorption temperatures of magnesium and lithium amide are given in table. As seen on table decomposition temperatures are very high and they all sensitive to moisture.

Table 6.5 : Storage density (wt%) and decomposition temperature of basic amides

Amide Type	**Storage Density, wt % H_2**	**^{o}C, Temperature**
$LiNH_2$	8,2	> 350
$NaNH_2$	5,1	500

7. ABSORPTION AND DESORPTION CHARECTERISTICS OF METAL HYDRIDES

7.1 Absorption And Desorption Characteristic

Hydrogen absorption/desorption is a thermo-chemical reaction. Hydrogen in gas form is absorbed or desorbed by solid metal hydride reactor. During absorption and desorption both depend on equilibrium pressure since:

$$Absorption.Force = P_{Supply(H_2)} - P_{Eq} \quad \textbf{(7.1)}$$

$$Desorption.Force = P_{Eq} - P_{ref(H_2)} \quad \textbf{(7.2)}$$

Equilibrium pressure changes parallel to bed temperature so temperature behavior must be analyzed. At the beginning of the absorption reaction, there is a difference between supply pressure and equilibrium bed pressure so reaction starts suddenly. Charging continues rapidly until its maximum point. After that, reaction speed slows down as a result temperature decreases. This causes a decline in equilibrium pressure. Again, a difference between supply pressure and equilibrium pressure occurs so absorption continues. At the end when bed temperature equals ambient bath temperature reaction stops. An example graphic is given below. Forde (2009) simulated reactor temperature of AB_5 type hydride and measured by three thermocouples at different places while charging pressure was 7 bar and reactor stands in a water bath at 20 ^{o}C. Initial reactor pressure was 0.5 bar.

Desorption of hydrogen occurs reversely. At the beginning of discharge, equilibrium pressure is higher than reference pressure. This is the cause of discharge. Hydrogen is transferred from metal hydride to reference volume rapidly, until reaching maximum point. During this time equilibrium pressure decreases with falling temperature. After that, reaction gets its maximum point and reaction decelerates which causes small increase in temperature.

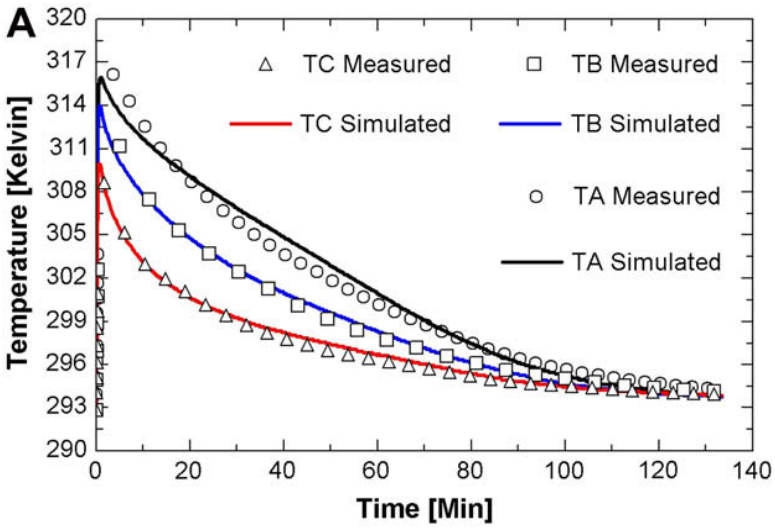


Figure 7.1 : Temperature change during absorption

As a consequence, equilibrium pressure increases, too. Driving force is generated and desorption continues until constant temperature. Forde (2009) obtained temperature trend of discharge by simulation and measurements. The trend is given in Figure. During reaction, discharge pressure is 2.5 bar and water bath temperature is 30 ^{o}C.

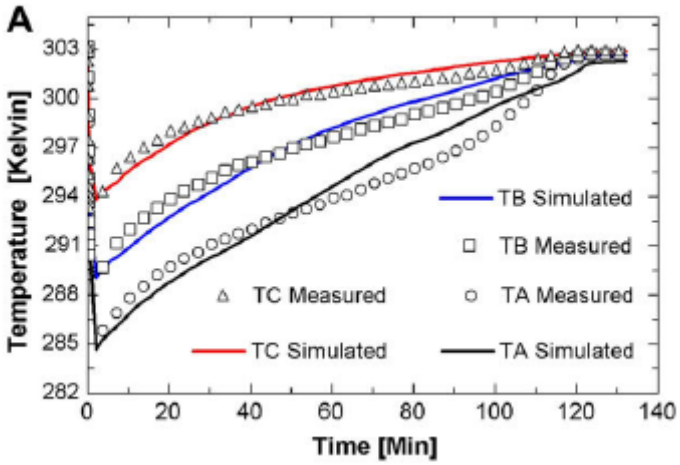


Figure 7.2 : Temperature change during desorption

7.2 Pressure Effect On Absorption

Hydrogen supply pressure is very important for absorption since driving force equals:

$$Absorbing.Force = P_{H_2} - P_{Eq} \quad \textbf{(7.3)}$$

For example, Forde (2009) analyzed AB_5 type metal hydride on absorption. At 6.5 bar supply pressure, required time is 20 minutes to fill 50% of capacity but at 10 bar this values decreases 10 min. Melloulia (2007) revealed that at constant time higher pressure not only decreases required time to fill the storage but also it increases the overall storage capacity.

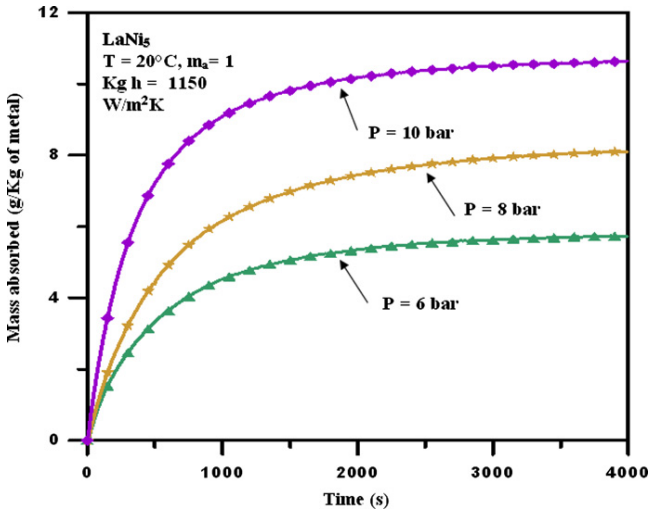


Figure 7.3 : Pressure effect on absorption

7.3 Temperature Effect On Absorption

The aim of charging is storing more hydrogen in lower volume by consuming minimum energy. Overall, the efficiency must be maximum and the cost, volume and weight of the hydrogen storage system must be minimum. So researchers have been examining ways that are more effective by calculating new mathematical models and they have been designing more beneficial storage systems.

$$M + xH_2 \Leftrightarrow MH_x + Heat \quad \textbf{(7.4)}$$

Hydrogen source of metal hydrides are generally high-pressurized gas tanks. The compressed hydrogen connects to metal hydride tank through the pressure regulator and hydrogen is transferred from supply to storage. Equation 7.3 is absorbing force of the reaction if equals zero reaction stops. If supply pressure is constant, this means that charging depends on storage conditions. Metal hydride storage as mentioned section 6.3.2 heats up during charging which increases storage pressure and finally

slows down the reaction. So, if metal hydride storage is cooled down on charging, its pressure does not increase, consequently absorption continues.

Mellouli (2007) made a spiral heat exchanger in metal hydride storage to cool down during charging. It was revealed that time required to fill the same amount of hydrogen by cooled system is 5 times lower than alone system. Moreover, Forde (2009) tested AB_5 type metal hydride storage with different bath temperatures. It was revealed that at 40 ^oC bath 33 min is needed while at 20 ^oC bath only 7 min is enough to fill 50% of storage capacity. As seen on graphic, Dhaou (2009) made a spiral heat exchanger and applied cooling water at different temperatures. It was reported that lower water temperature improves absorbed hydrogen.

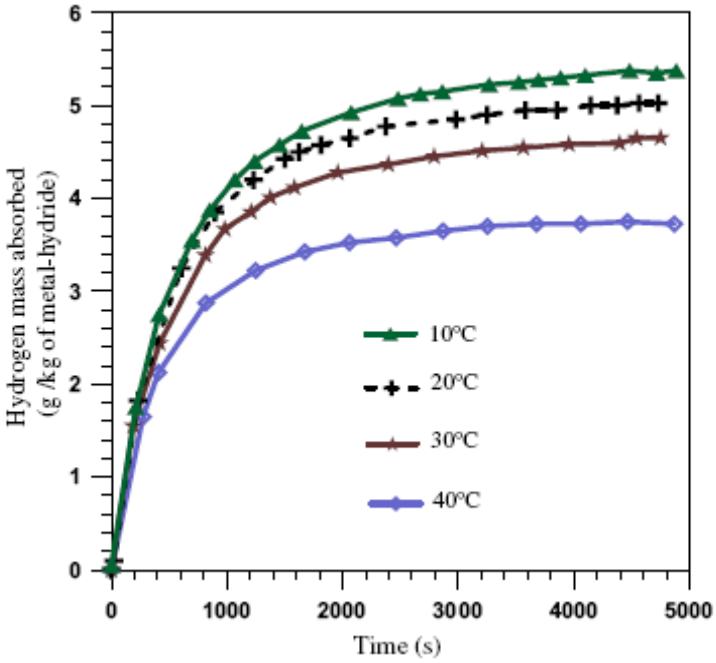


Figure 7.4 : Effect of temperature on absorption

Cooling water decreases average bed temperature as a result equilibrium pressure declines. If equilibrium pressure declines, the difference between supply pressure and equilibrium pressure will rise. This means that driving force, which enhances absorption will increase, too.

7.4 Pressure Effect On Desorption

During desorption hydrogen flows from storage to reference volume. This flow can be expressed like electrical current, which is caused by potential difference. Like, electrical current hydrogen tends to move from higher pressure to lower pressure.

Dhaou (2009) experienced desorbed hydrogen mass at different pressurized reference volumes. It was proved that the desorbed hydrogen mass increases at lower reference volume.

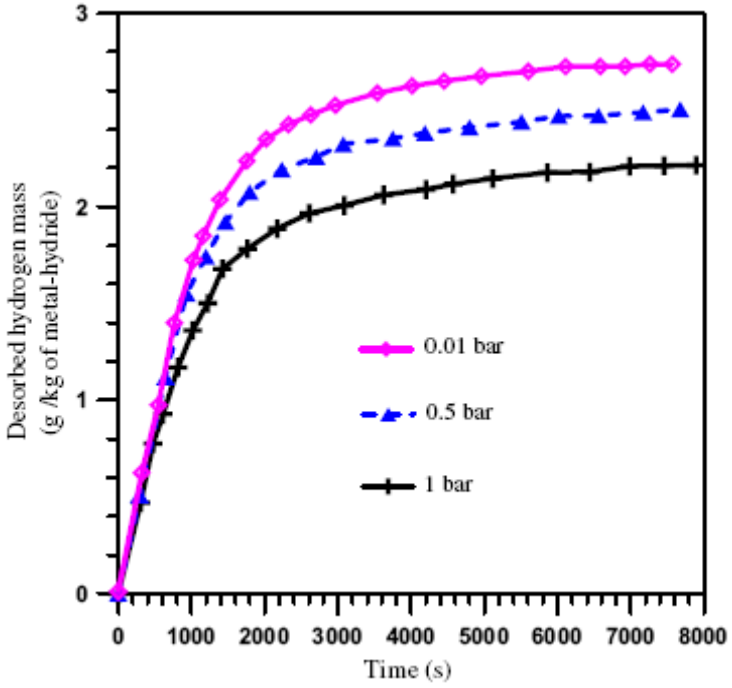


Figure 7.5 : Reference pressure effect on absorption

7.5 Temperature Effect On Desorption

The idea, heating provides better desorption has been supported by many technical researches. The reason is very simple: Decomposition of metal hydride is an endothermic reaction so it needs heat. Forde (2009) examined an AB_5 type metal hydride's desorption performance at different bath temperatures; 20 ^{o}C, 30 ^{o}C and 40 ^{o}C. Results were interesting; 85% of stored hydrogen could be released at 20 ^{o}C and storage efficiency dramatically increased to 95% at 30 ^{o}C, but at 40 ^{o}C efficiency didn't change. On the other hand, higher temperature always reaches the same point faster than lower temperature.

Dhaou (2009) investigated $LaNi_5$ desorption performance by adding a heat exchanger mechanism in storage bed. Water at different temperatures such as 60, 50, 40 and 30 ^{o}C was used as a heating liquid. Results were positive: Desorbed mass increased and desorption time decreased by higher temperature. MgH_2 was analyzed with catalyst at 200, 250 ^{o}C and without catalyst at 200, 250, 275 ^{o}C. It was indicated that reaction

without catalyst, at 200 ^{o}C, desorption rate was nearly 0% without catalyst but at 275 ^{o}C, desorbed mass is about 7% . (Sakintuna, 2006). Lastly, Jain (2010) searched temperature effect on decomposition of $NaAlH_4$. It was obtained that desorption reaction suddenly increases by changing temperature from 160 ^{o}C to 220 ^{o}C.

Jiang (2004) made a sample modeling and simulation study, which is similar to the topic of this thesis. A fuel cell and metal hydride bed were modeled and thermally coupled with each other in simulation. To make a comparison another system without thermally coupled was simulated, too. Removed heat of fuel cell was transferred to hydride storage. In conclusion, it was claimed that the thermally coupled system could supply power longer than other system. Thermally coupling improved the released/stored efficiency of metal hydride storage. Because heating increased storage temperature and equilibrium pressure, so coupled system could force hydrogen discharging longer than not coupled system.

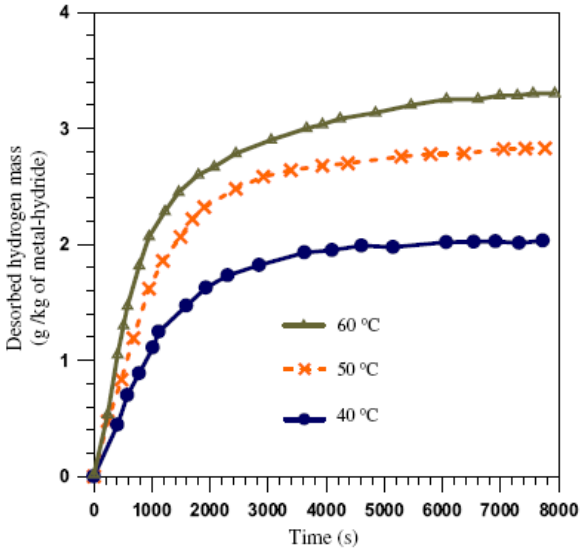


Figure 7.6 : Temperature effect on desorption

8. PROPOSED SYSTEM TO IMPROVE DESORPTION EFFICIENCY OF THE METAL HYDRIDE STORAGE

8.1 System Overview

Last chapter analyzed that the desorption efficiency of a metal hydride storage can be improved by heating. A closed-circuit heat transfer system is proposed to apply on hydrogen fuel cell powered electric vehicle to increase its range by the same storage.

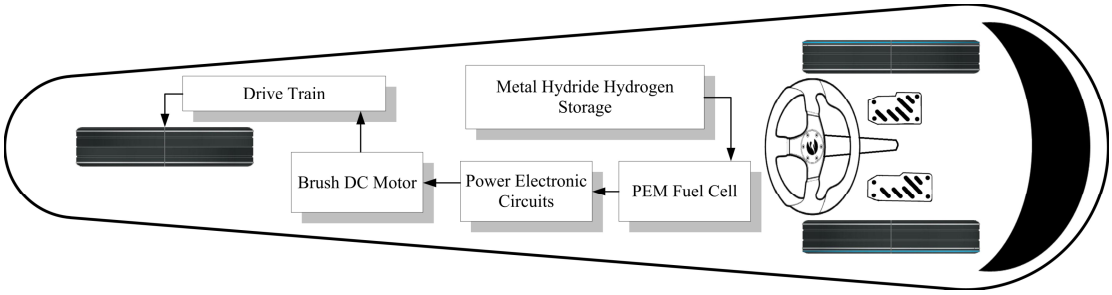


Figure 8.1 : Block scheme of the hydrogen fuel cell vehicle

The hydrogen fuel cell vehicle has three wheels and mechanical power is applied on the rear wheel. Mechanical power, generated by a brush type DC motor is transferred to the rear-wheel by the virtue of drive train. Electrical energy is generated by a PEM fuel cell and converted by power electronic circuits. The nominal values of fuel cell are: 26 VDC, 46 A and 1200W. Specifications of the PEMFC is given in appendices. The PEMFC uses ambient air to provide its oxygen need and hydrogen is supplied by a group of metal hydride storage. There are three metal hydride storages used in vehicle and a storage is about 6.5 kg (empty) and 2.5 lt.

Block scheme of the proposed closed-circuit heat transfer system is given in Figure 8.2. The proposed system contains mainly three main parts; the radiator, the vessel and the pump. The aim of proposed system is circulating the water by the water-pump from the radiator to the vessel and vessel to radiator. Normally, during desorption operation, the PEM fuel cell works and emits heat, on the other hand; the metal hydride storage cools down (as mentioned in section 7.1), and cooling

decreases its equilibrium pressure. If equilibrium pressure decreases, the reaction will slow down until it equals the PEM fuel cell's shut down pressure.

The purpose of closed-circuit heat transfer system is to collect the PEM fuel cell's removed heat and transfer it to metal hydride storage. Besides, the aim of proposed system is to increase or not to allow metal hydride's temperature to decrease, by this way; desorption hydrogen amount will be increased and desorption efficiency will be improved.

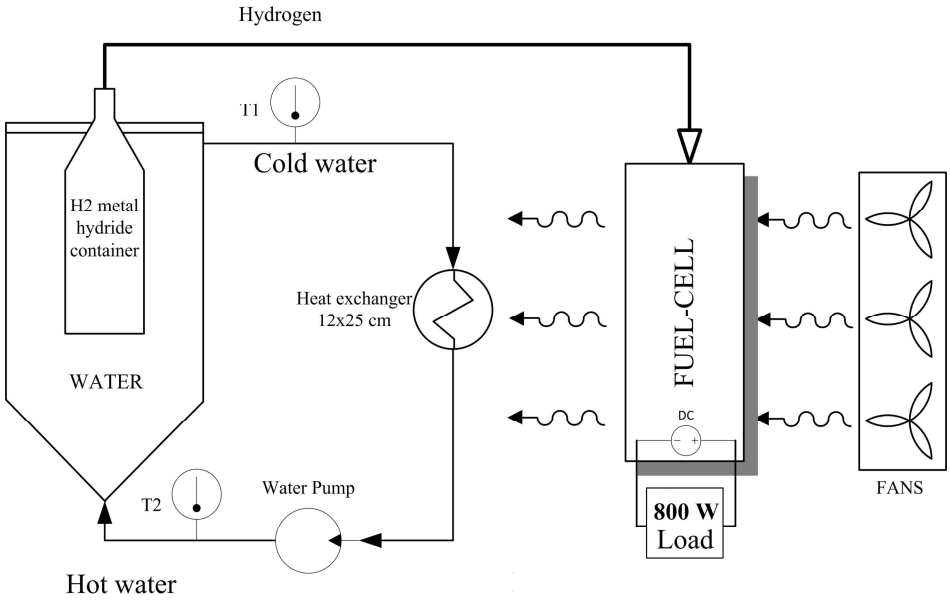


Figure 8.2 : Block scheme of the proposed heat transfer system

9. EXPERIMENTAL SETUP

To see the effect of proposed system three experiments setup were realized. Firstly, the metal hydride storage was tested with proposed system. Secondly, the same storage was tested without proposed system as normal operation. Lastly, the storage, which was tested in normal operation and was not able to deliver more hydrogen, tested with proposed system. Before the first and second test, metal hydride storage was put in a fully iced container and it was filled from compressed hydrogen source at 11.6 bar pressure until equilibrium state. To get comparable results both the first and second test were started from 10 bar and continued to shut-down point.

9.1 With Proposed System

Block scheme and picture of proposed system are given in Figure 9.1 and Figure 9.2.

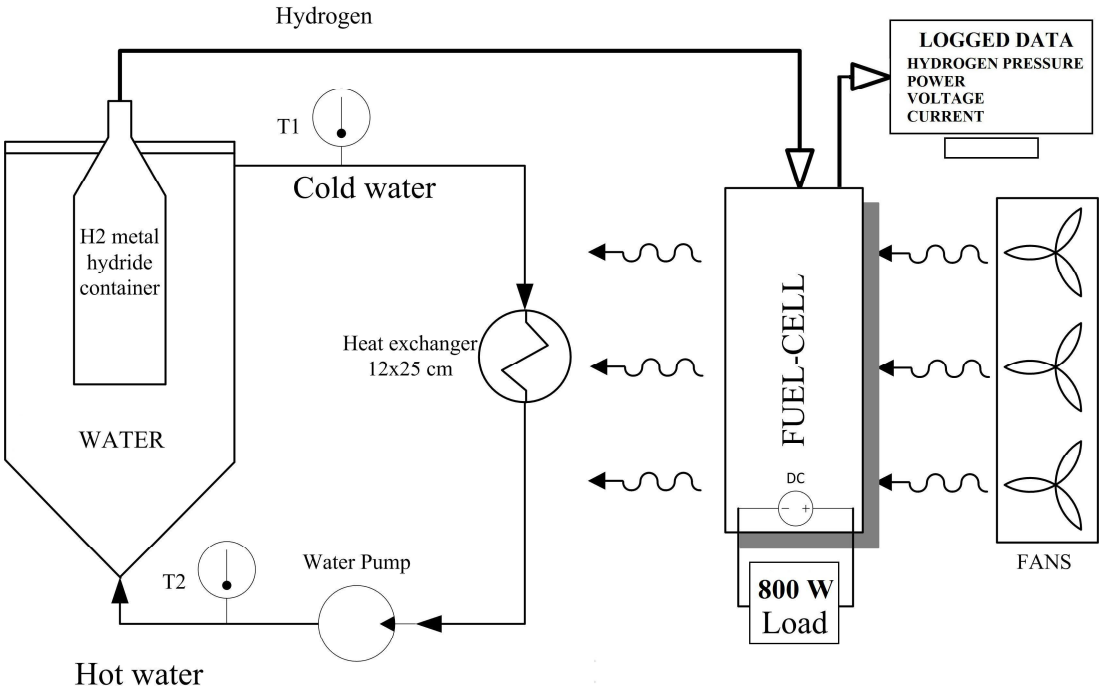


Figure 9.1 : Experimental setup block scheme of the proposed system

Figure 9.2 : Realized proposed system

Firstly, a radiator was used to collect fuel cells removed heat. It has cold water inlet and hot water outlet. Dimensions of the radiator, 250mm(l)x120mm(w)x30mm(h), were chosen to be fitted on the fuel cell's removed hot air exit side. The second equipment is the vessel, in which metal hydride storage inserted. It has a hot water inlet and cold water outlet. The volume and shape of the vessel were chosen as suitable as the metal hydride storage. The water was preferred as heating liquid because it has good heat conductance and high specific heat. Moreover, pumping water is an easy process, which was performed by a plastic housing water pump. Connections -vessel to pump, pump to radiator and radiator to vessel- of closed-circuit heat transfer system were made by plastic flexible pipes. Steps of the first experiment listed below:

1- Software and power connections of PEM fuel cell were done.

2- The load, 800W, was connected to output of the PEM fuel cell.

3- The radiator was fitted on the PEM fuel cell's hot air outlet.

4- Thermocouples were mounted on hot water inlet and cold water outlet of the vessel.

5- Pipe connections were done.

6- The metal hydride storage was put in the vessel.

7- Hydrogen connection between metal hydride storage and PEM fuel cell were made.

8- Ambient air was checked by hydrogen leakage sensor.

9- The PEM fuel cell was started to run.

10- Voltage, current and power outputs of the PEM fuel cell (and also load) were logged by the software.

11- Hydrogen pressure of metal hydride storage was logged by the software.

12- Inlet and outlet water temperatures were measured by thermocouples, read by multi-meter and values were noted manually.

13- Operation and data logging continued until the PEM fuel cell shut downs the operation because of lack of fuel (hydrogen).

9.2 Without Proposed System

Block scheme and picture of realized experimental setup are given in Figure 9.3 and Figure 9.4.

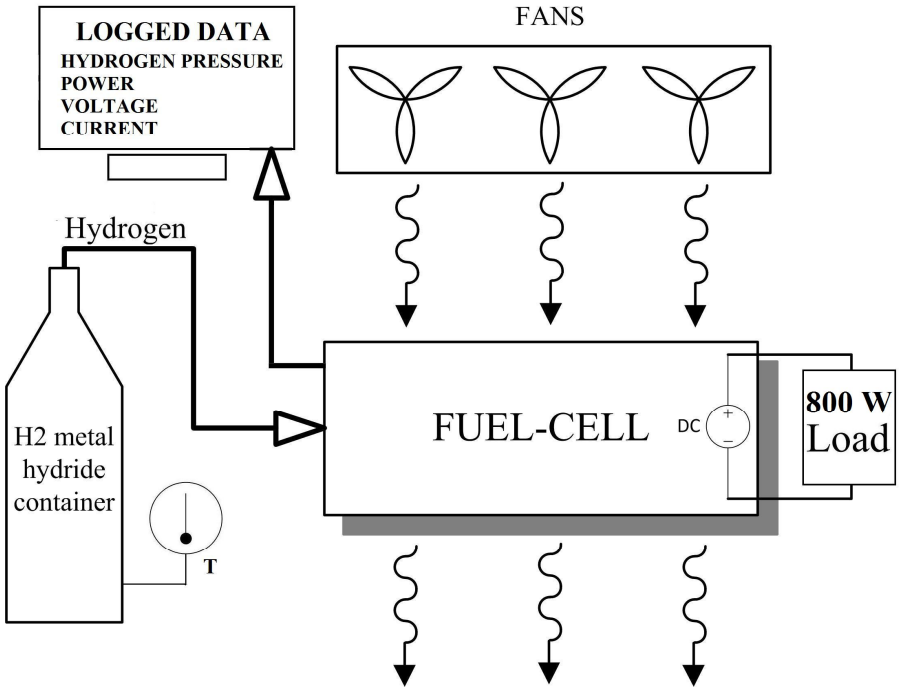


Figure 9.3 : Experimental setup block scheme of normal operation

Figure 9.4 : Realized normal operation (without proposed system)

Before this experiment, as stated above, metal hydride storage filled from compressed hydrogen source. Steps of the first experiment listed below:

1- Software and power connections of PEM fuel cell were done.

2- The load, 800W, was connected to output of the PEM fuel cell.

3- A thermocouple was mounted on surface of the metal hydride storage.

4- Hydrogen connection between metal hydride storage and PEM fuel cell were done.

5- Ambient air was checked by hydrogen leakage sensor.

6- The PEM fuel cell was started to run.

7- Voltage, current and power outputs of the PEM fuel cell (and also load) were logged by the software.

8- Hydrogen pressure of metal hydride storage was logged by the software.

9- Temperature of the metal hydride storage was measured by thermocouples, read by multi-meter and values were noted manually.

10- Operation and data logging continued until the PEM fuel cell shut downs the operation because of lack of fuel (hydrogen).

9.3 With Proposed System For Squeezed Storage

As stated above, the PEM fuel cell can measure supply hydrogen pressure. It works until hydrogen pressure decreases below its minimum requirement point. At that point, for the PEMFC this means “The storage is empty”, the PEM fuel cell shuts down the operation. For this third experimental setup the metal hydride storage, which was used in second test (without proposed system), was directly tested with proposed system. All of the steps of first experiment were done. So they were not written in here.

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10. RESULTS

10.1 Experimental Results With Proposed System

For this test, metal hydride storage is filled at 11.6 bar and emptied until 10 bar. The fuel cell operation was started at 10 bar storage pressure and then it was observed that storage pressure suddenly increased to 10.4 bar. Before water circulation, water temperature was nearly 24 ^{o}C but after, the temperature started to increase smoothly to 27 ^{o}C. The metal hydride storage could feed the PEM fuel cell, which was running at 800 Watts output power. The pressure of the metal hydride decreased from 10 bar to 0.5 bar in 61 minutes and the PEM fuel cell run the 800 W load for this period without any interruption. Temperature and pressure graphic of metal hydride storage is given in Figure 10.1 and power output of the PEM fuel cell is given in figure 10.

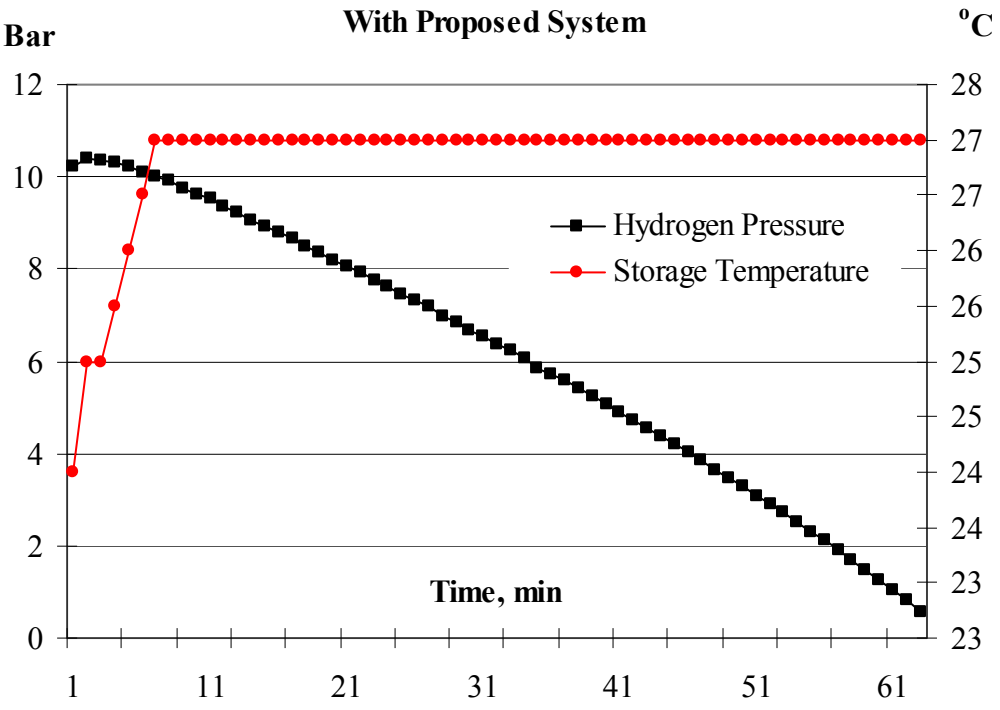

Figure 10.1 : Hydrogen pressure and storage temperature @ 800 W fuel cell load with proposed system

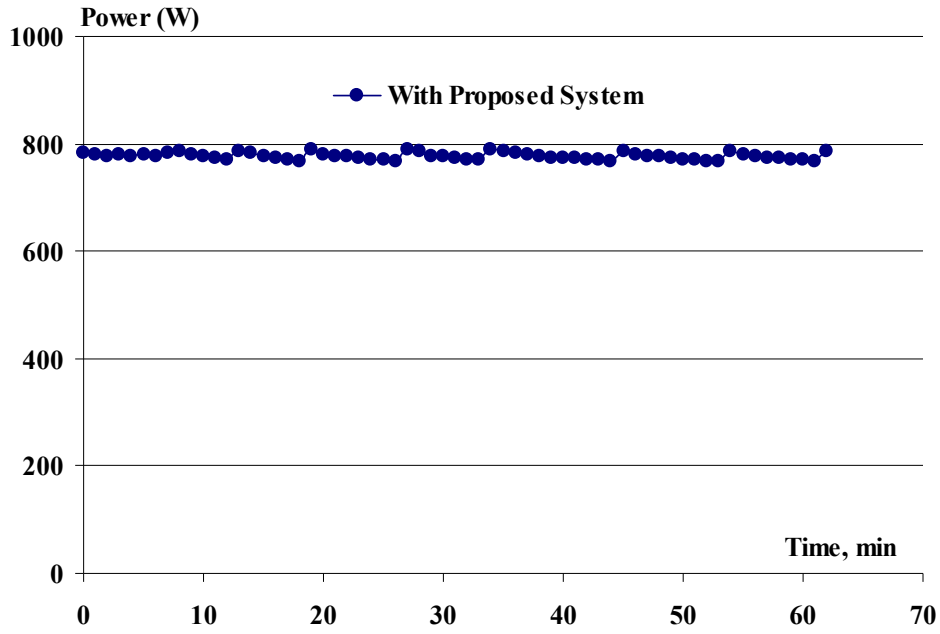

Figure 10.2 : The PEM fuel cell output power during desorption of MH storage with proposed system

10.2 Experimental Results Without Proposed System

From the beginning of the operation, the metal hydride storage started to cool down rapidly. Storage temperature was measured by a thermocouple, which was mounted on its surface and isolated from ambient. Figure 10.3 shows the temperature and pressure of storage during operation. The PEM fuel cell continued to feed 800 W output power for only 18 minutes, (Figure 10.4) until supply pressure dropped to 0.8 bar. Figure 10.5 reveals that when the PEM fuel cell closed down the operation, the temperature of storage was 0 ^{o}C and the surface of storage was frost.

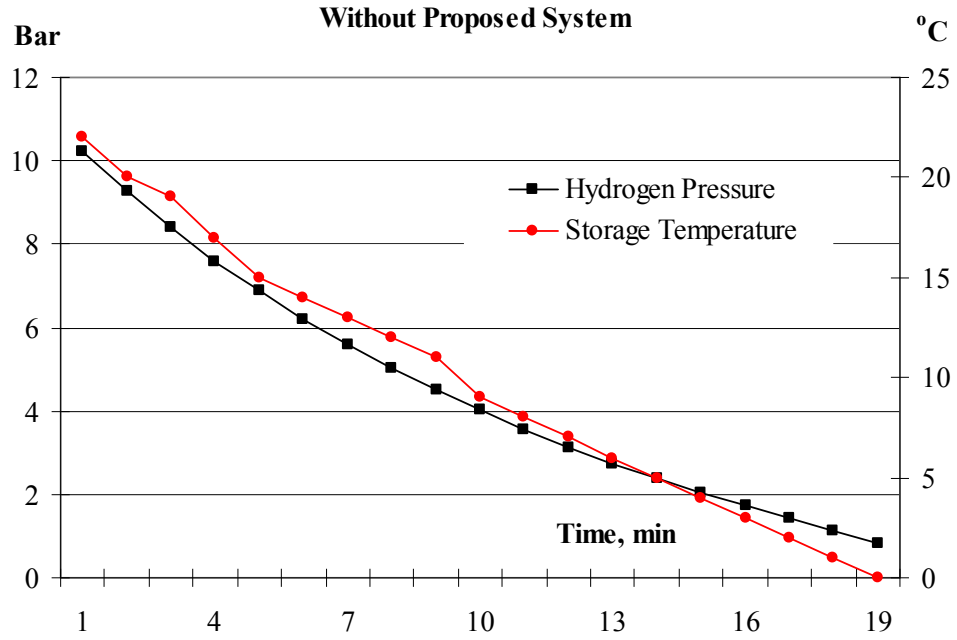

Figure 10.3 : Hydrogen pressure and storage temperature @ 800 W fuel cell load without proposed system (normal operation)

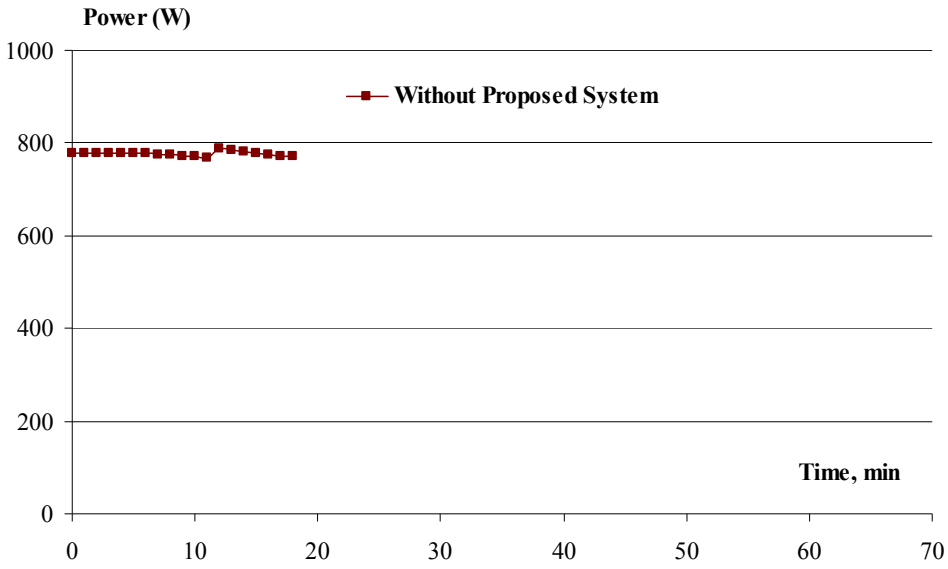

Figure 10.4 : The PEM fuel cell output power during desorption of MH storage without proposed system (normal operation)

Figure 10.5 : Iced metal hydride storage during desorption without proposed system

10.3 Experimental Results With Proposed System For Squeezed Storage

The (iced) storage, after the experiment without proposed system (normal operation), was inserted into the vessel and heat transfer system was switched on. Result graphics are given below. The "empty" (supposed by the PEMFC) and "iced" storage continued to feed the PEM fuel cell 50 minutes at 800 W output load.

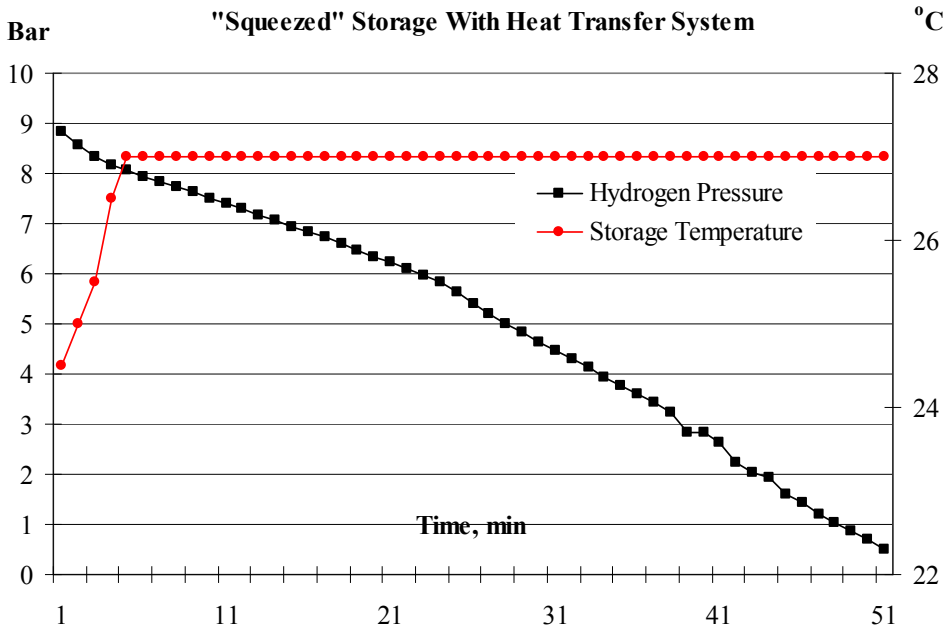

Figure 10.6 : Hydrogen pressure and storage temperature @ 800 W fuel cell load

with proposed system (for “squeezed” storage)

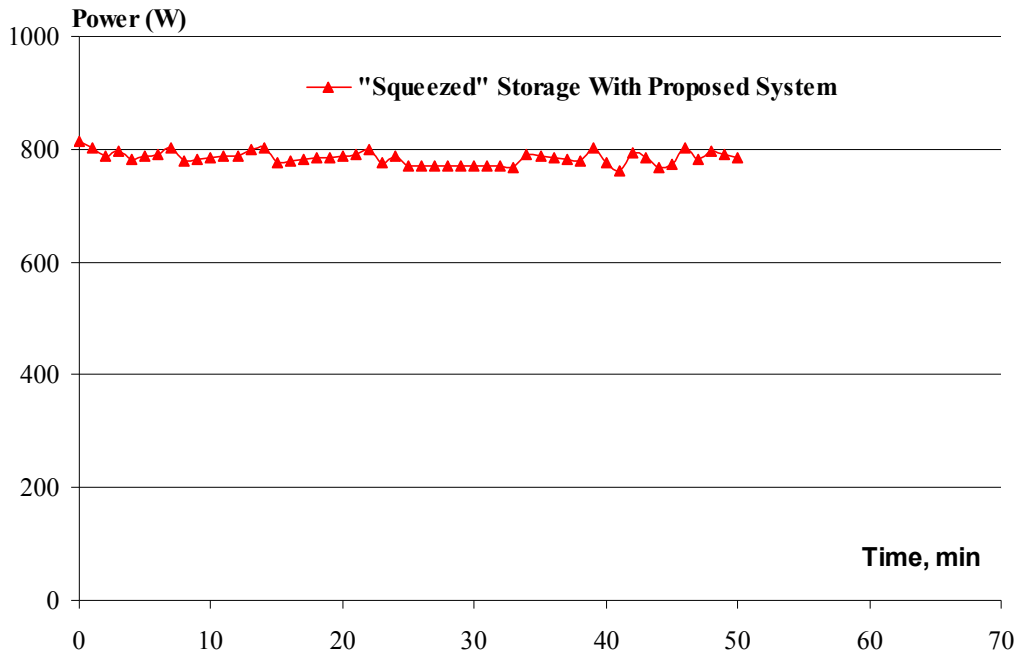

Figure 10.7 : The PEM fuel cell output power during desorption of MH storage with proposed system (for “squeezed” storage)

10.4 General Results and Recommendations

The first and second experiments show that proposed system significantly increased the desorbed hydrogen amount from the metal hydride storage. For normal operation, while the metal hydride storage can supply hydrogen for the PEM fuel cell, operating at 800 W load power, for only 18 minutes; with proposed system this time is extended to 61 minutes. Although it is supposed by PEMFC that metal hydride storage is empty, the third experiment shows there is still some hydrogen in the storage.

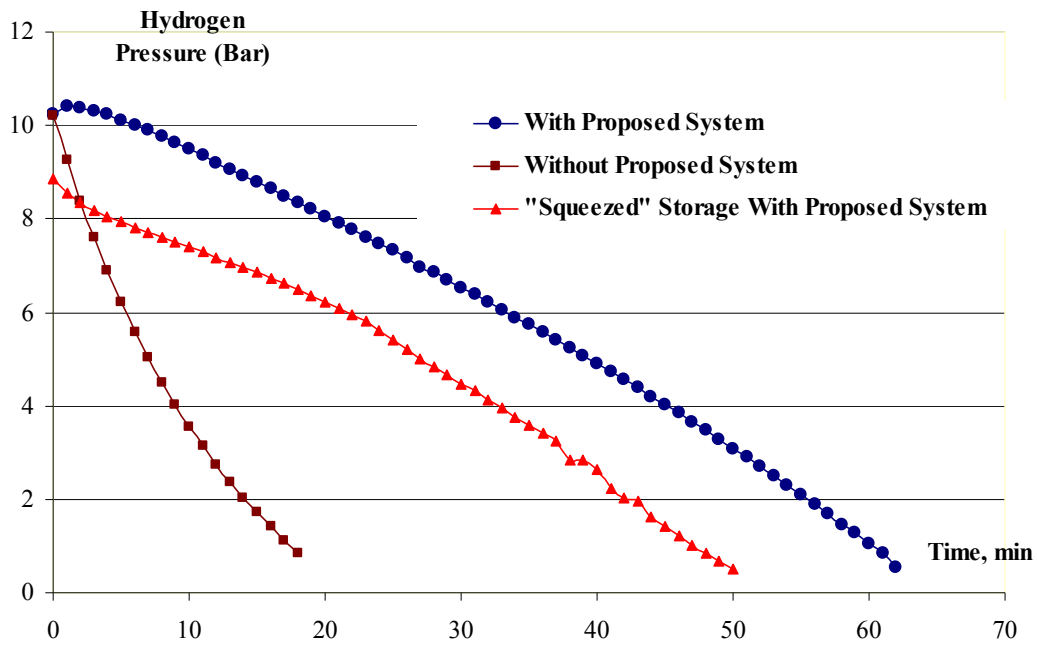

Figure 10.8 : The MH Storage pressure @800 W fuel cell load with and without proposed heat transfer system

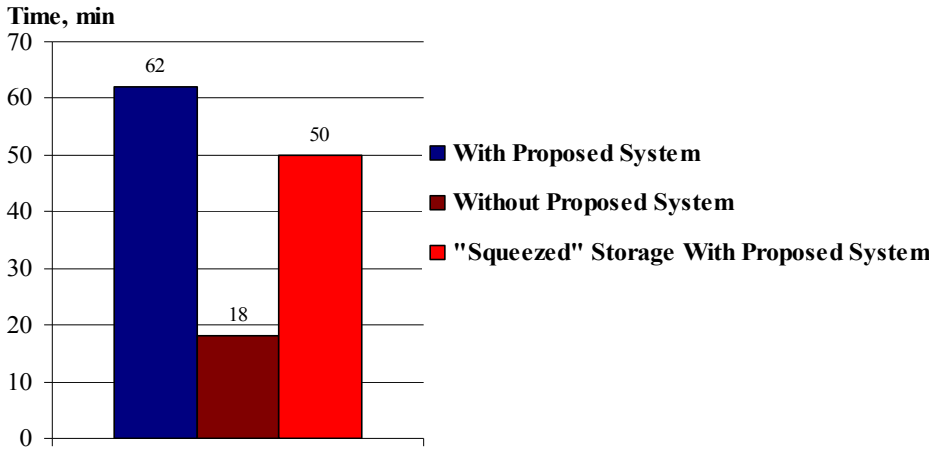

Figure 10.9: Time period in which MH storage could supply hydrogen for the fuel cell at 800W output poweR

In conclusion, experiments prove that proposed system works very-well and improves desorption efficiency and inreases desorbed hydrogen. By this way, the range of the vehicle can be inceased. Moeover, it is believed that the better performance can be obtained by using an optimum radiator and vessel with loseless piping at optimum flow rate and by using extended heat sources on a vehicle.

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APPENDICES

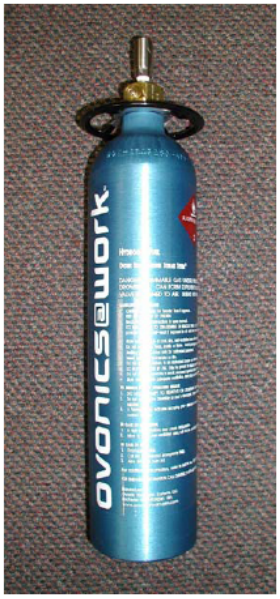
APPENDIX A.1 : PEM Fuel Cell Specifications
APPENDIX A.2 : Metal Hydride Hydrogen Specifications
APPENDIX A.3 : Experiment Data

APPENDIX A.1

OUTPUTS	Requirement	Definition	Quantity
Power[1]	Rated Power	Capacity at Standard Conditions, BOL	1200 W
	Voltage	Operating voltage range	22 V to 50 V
		Voltage at Rated Power	26 V
	Start-up Time	Minimum time to achieve Rated Power from a Cold Start condition	2 minutes
Emissions	Noise	Maximum noise emission at 1m	72 dBA
	Water	Maximum quantity of liquid water produced at Rated Power	870 mL/hr
Physical	Dimensions	L x W x H	56 x 25 x 33cm
	Mass	Total system mass	13 kg
Lifetime	Operating Life	Minimum number of operating hours before EOL	1500 hours
	Cyclic Life	Minimum number of start-up & shut-down cycles before EOL	500
	Shelf Life	Minimum storage (non-operation) before EOL	2 years
INPUTS	**Requirement**	**Definition**	**Quantity**
Fuel	Purity	Lowest acceptable concentration of hydrogen	99.99% H_2 (vol)
	Pressure	Allowable range of inlet supply pressure[2]	70 – 1720 kPa(g)
	Acceptable Impurities	Maximum total inert fluids (including helium, argon, nitrogen and water vapour)	0.01% (vol)
		Maximum CO and CO_2 combined	2 ppm (vol)
		Maximum total hydrocarbon	1 ppm (vol)
		Maximum oxygen	500 ppm (vol)
	Consumption	Maximum fuel consumption at Rated Power	<18.5 SLPM
Power Conditioning	Current Ripple	Maximum acceptable current ripple at 120 Hz, with respect to average DC net output current	24.7% RMS 35% peak-peak
DC Power Supply	Voltage	Allowable range of input voltage	18 V to 30 V
	Power	Maximum power draw during start-up	60 W
Operating Environment	Location	Acceptable locations for use	Indoors & Outdoors
	Temperature Range	Range of acceptable ambient, cooling air and oxidant air temperatures	3°C - 40°C
	Relative Humidity	Range of acceptable ambient relative humidity	0% - 95% (non-condensing)
	EMI Tolerance	Tolerant to and operates safely in the EMI environment specified by	UL 991

APPENDIX A.2

Ovonic® Solid Hydrogen Storage Canister
Model 85G250B-NPT / 85G555B-NPT

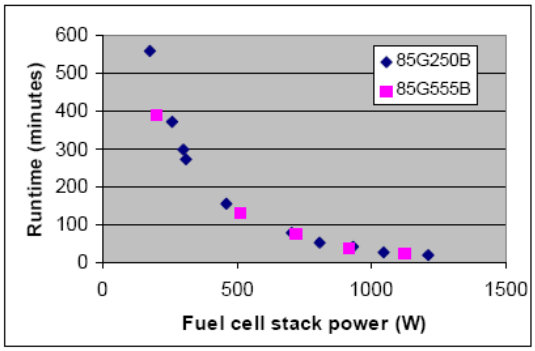


Shown with optional lifting ring and quick-connect coupling. Actual appearance may vary .

Technical Specifications

	Standard high-capacity model 85G250B-NPT	International "air-shippable"* model 85G555B-NPT
Hydrogen storage capacity, nominal	80 grams / 900 std. liters (condition dependent)	76 grams / 850 std. liters (condition dependent)
Diameter	3.5 in. / 89 mm	
Length	15.1 in. / 384 mm (16.5 in. / 419 mm w/ coupling)	
Weight	14 lbs. / 6.5 kg	
Rated discharge	6 slpm / 600 watts	
Re-filling	Charges in approximately 8 hours at 250psig In flowing ambient air.	
Operating temperature	32-167°F / 0-75°C	
Storage temperature	-20-130°F / -29-54°C	
		*for air shipment, all hydrogen must be desorbed

Typical desorption performance in RT air flowing at 6 m/sec



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APPENDIX A.3

With Proposed System							
Time (min)	**Voltage DC (V)**	**Current DC (A)**	**Power (W)**	**Hydrogen Pressure (Bar)**	**Inlet W.T.^{o}C**	**Outlet W.T. ^{o}C**	**Average V.T. ^{o}C**
0	32,80	23,95	782	10,23	24	24	24
1	32,80	23,94	779	10,40	25	25	25
2	32,75	23,90	778	10,37	25	25	25
3	32,80	23,89	781	10,31	26	25	26
4	32,70	23,85	776	10,23	26	26	26
5	32,75	23,92	780	10,10	27	26	27
6	32,75	23,88	777	10,02	27	27	27
7	32,70	23,85	783	9,90	27	27	27
8	32,75	23,87	785	9,76	27	27	27
9	32,75	23,88	779	9,62	27	27	27
10	32,70	23,86	776	9,51	27	27	27
11	32,70	23,86	775	9,37	27	27	27
12	32,70	23,84	771	9,21	27	27	27
13	32,79	24,03	787	9,06	27	27	27
14	32,75	23,86	782	8,93	27	27	27
15	32,65	23,81	777	8,79	27	27	27
16	32,70	23,82	773	8,65	27	27	27
17	32,70	23,79	772	8,50	27	27	27
18	32,65	23,79	768	8,36	27	27	27
19	32,70	23,81	788	8,20	27	27	27
20	32,65	23,77	781	8,06	27	27	27
21	32,65	23,81	778	7,92	27	27	27
22	32,65	23,80	777	7,77	27	27	27
23	32,65	23,75	774	7,62	27	27	27
24	32,60	23,73	772	7,46	27	27	27
25	32,60	23,70	769	7,33	27	27	27
26	32,60	23,72	768	7,17	27	27	27
27	32,65	23,80	788	6,98	27	27	27
28	32,60	23,79	786	6,85	27	27	27
29	32,60	23,74	778	6,69	27	27	27
30	32,55	23,75	776	6,54	27	27	27
31	32,50	23,72	773	6,38	27	27	27
32	32,50	23,73	770	6,23	27	27	27
33	32,60	23,74	769	6,06	27	27	27
34	32,60	23,72	788	5,87	27	27	27
35	32,50	23,80	787	5,73	27	27	27
36	32,50	23,73	783	5,57	27	27	27
37	32,45	23,72	779	5,40	27	27	27
38	32,55	23,72	776	5,24	27	27	27
39	32,40	23,70	775	5,08	27	27	27
40	32,45	23,70	774	4,90	27	27	27
41	32,40	23,67	773	4,74	27	27	27
42	32,40	23,69	770	4,56	27	27	27
43	32,45	23,63	769	4,38	27	27	27

With Proposed System							
Time (min)	**Voltage DC (V)**	**Current DC (A)**	**Power (W)**	**Hydrogen Pressure (Bar)**	**Inlet W.T.^{o}C**	**Outlet W.T. ^{o}C**	**Average V.T. ^{o}C**
44	32,45	23,67	767	4,20	27	27	27
45	32,50	23,70	787	4,03	27	27	27
46	32,55	23,70	781	3,84	27	27	27
47	32,35	23,61	777	3,66	27	27	27
48	32,45	23,66	776	3,47	27	27	27
49	32,40	23,62	774	3,28	27	27	27
50	32,40	23,60	772	3,09	27	27	27
51	32,30	23,60	769	2,90	27	27	27
52	32,30	23,54	767	2,71	27	27	27
53	32,40	23,59	766	2,51	27	27	27
54	32,35	23,63	786	2,31	27	27	27
55	32,40	23,60	779	2,11	27	27	27
56	32,40	23,58	776	1,90	27	27	27
57	32,35	23,58	775	1,69	27	27	27
58	32,30	23,53	773	1,47	27	27	27
59	32,30	23,54	771	1,27	27	27	27
60	32,25	23,53	769	1,06	27	27	27
61	32,35	23,48	767	0,84	27	27	27
62	32,30	23,56	786	0,55	27	27	27
W.T : Water Temperature ; V.T : Vessel Temperature							

Without Proposed System					
Time (min)	**Voltage DC (V)**	**Current DC (A)**	**Power (W)**	**Hydrogen Pressure (Bar)**	**Storage Temp. oC**
0	33,39	23,98	777	10,21	22
1	33,39	23,96	779	9,26	20
2	33,29	23,91	779	8,4	19
3	33,19	23,89	779	7,6	17
4	33,09	23,88	779	6,88	15
5	33,04	23,8	777	6,21	14
6	32,99	23,8	777	5,59	13
7	32,99	23,77	776	5,03	12
8	32,89	23,74	774	4,51	11
9	32,84	23,7	773	4,01	9
10	32,75	23,65	771	3,56	8
11	32,75	23,67	769	3,14	7
12	32,89	23,67	789	2,74	6
13	32,79	23,69	785	2,38	5
14	32,84	23,63	781	2,04	4
15	32,7	23,57	778	1,73	3
16	32,7	23,54	776	1,42	2
17	32,65	23,55	773	1,13	1
18	32,55	23,53	770	0,84	0

"Squeezed" Storage With Proposed System							
Time (min)	**Voltage DC (V)**	**Current DC (A)**	**Power (W)**	**Hydrogen Pressure (Bar)**	**Inlet W.T.°C**	**Outlet W.T. °C**	**Average V.T. °C**
0	35,06	21,76	814	8,84	25	24	25
1	34,72	21,56	803	8,56	25	25	25
2	34,47	21,45	787	8,35	26	25	26
3	34,32	21,39	796	8,18	27	26	27
4	34,18	21,28	781	8,06	27	27	27
5	34,08	21,28	787	7,94	27	27	27
6	33,93	21,3	791	7,82	27	27	27
7	34,03	21,27	803	7,72	27	27	27
8	33,73	21,18	779	7,62	27	27	27
9	33,68	21,14	782	7,5	27	27	27
10	33,68	21,13	785	7,4	27	27	27
11	33,78	21,17	787	7,29	27	27	27
12	33,63	21,19	789	7,17	27	27	27
13	33,73	21,13	800	7,06	27	27	27
14	33,73	21,17	801	6,95	27	27	27
15	33,58	21,1	777	6,85	27	27	27
16	33,58	21,07	779	6,72	27	27	27
17	33,53	21,1	782	6,61	27	27	27
18	33,63	21,03	784	6,48	27	27	27
19	33,58	21,1	785	6,35	27	27	27
20	33,63	21,11	788	6,23	27	27	27
21	33,53	21,1	792	6,1	27	27	27
22	33,58	21,13	799	5,96	27	27	27
23	33,53	21,05	777	5,83	27	27	27
24	32,5	24,85	789	5,62	27	27	27
25	32,4	24,75	769	5,4	27	27	27
26	32,45	24,83	769	5,2	27	27	27
27	32,5	24,85	769	5,01	27	27	27
28	32,5	24,82	770	4,82	27	27	27
29	32,6	24,8	770	4,65	27	27	27
30	32,5	24,81	769	4,47	27	27	27
31	32,55	24,8	769	4,31	27	27	27
32	32,45	24,79	769	4,13	27	27	27
33	32,45	24,8	767	3,95	27	27	27
34	32,5	24,83	791	3,76	27	27	27
35	32,6	24,83	789	3,6	27	27	27
36	32,6	24,86	785	3,42	27	27	27
37	32,5	24,78	781	3,24	27	27	27
38	32,5	24,79	780	2,84	27	27	27
39	32,4	24,77	803	2,83	27	27	27
40	30,76	24,86	775	2,65	27	27	27
41	30,63	24,83	763	2,22	27	27	27
42	34,42	21,19	794	2,03	27	27	27
43	34,08	21,02	785	1,95	27	27	27
44	33,35	23,56	768	1,61	27	27	27
45	33,38	23,61	773	1,43	27	27	27
46	33,75	23,81	801	1,21	27	27	27
47	33,44	23,52	781	1,02	27	27	27

"Squeezed" Storage With Proposed System							
Time (min)	**Voltage DC (V)**	**Current DC (A)**	**Power (W)**	**Hydrogen Pressure (Bar)**	**Inlet W.T.^{o}C**	**Outlet W.T. ^{o}C**	**Average V.T. ^{o}C**
48	33,39	23,54	797	0,86	27	27	27
49	33,29	23,44	792	0,69	27	27	27
50	33,29	23,52	786	0,51	27	27	27
"Squeezed" Storage With Proposed System							

CURRICULUM VITAE

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